Advanced Method for Measurement of the Solid Carbonaceous (Soot) Component of Mobile Source Particulate Matter

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LII Technology Licensed from NRC, Canada

Greg Smallwood, Ph.D. and David Snelling, Ph.D.

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LII Development Supported by: NASA, EPA, NIST SBIR Phase I and II grants

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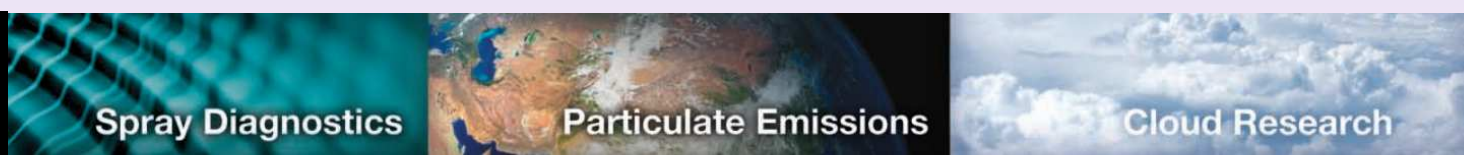


Air Quality/Health

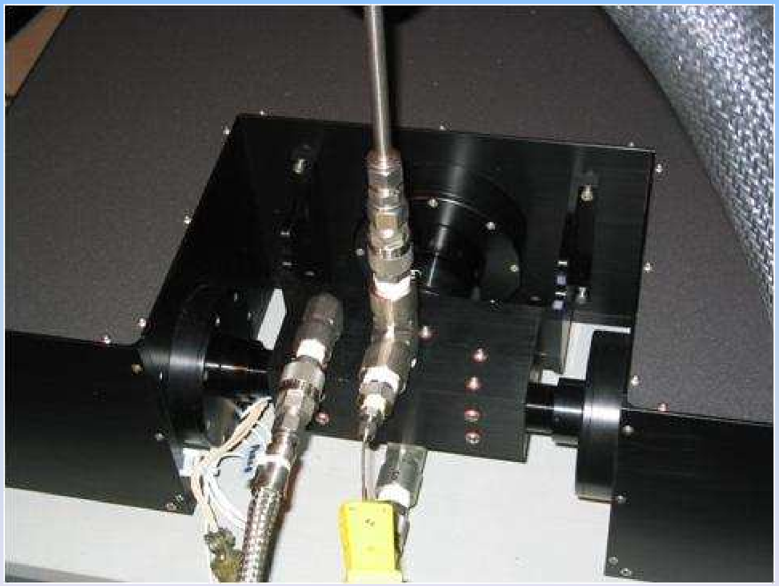
Improvements have significant benefits

Why is soot a serious concern?

- **Research indicates soot is implicated directly in numerous health problems**
- **Microscopic soot particles are among the most harmful components of air pollution**
- **Black carbon (soot) is a key contributor to radiative forcing, important to climate change**
- **New regulations in California significantly limit the allowable particulate emissions from diesel engines**
- **Regulations require means for determining compliance**

Outline

- Background
  - introduction
  - reduced PM emissions a problem for gravimetric methods
  - conventional laser-induced incandescence (LII) method
- Auto-compensating laser-induced incandescence (AC-LII) method
  - innovations
  - theory
  - experimental
- Applications
  - engine dyno measurements
  - chassis dyno measurements
  - on-road measurements
  - gas turbine measurements



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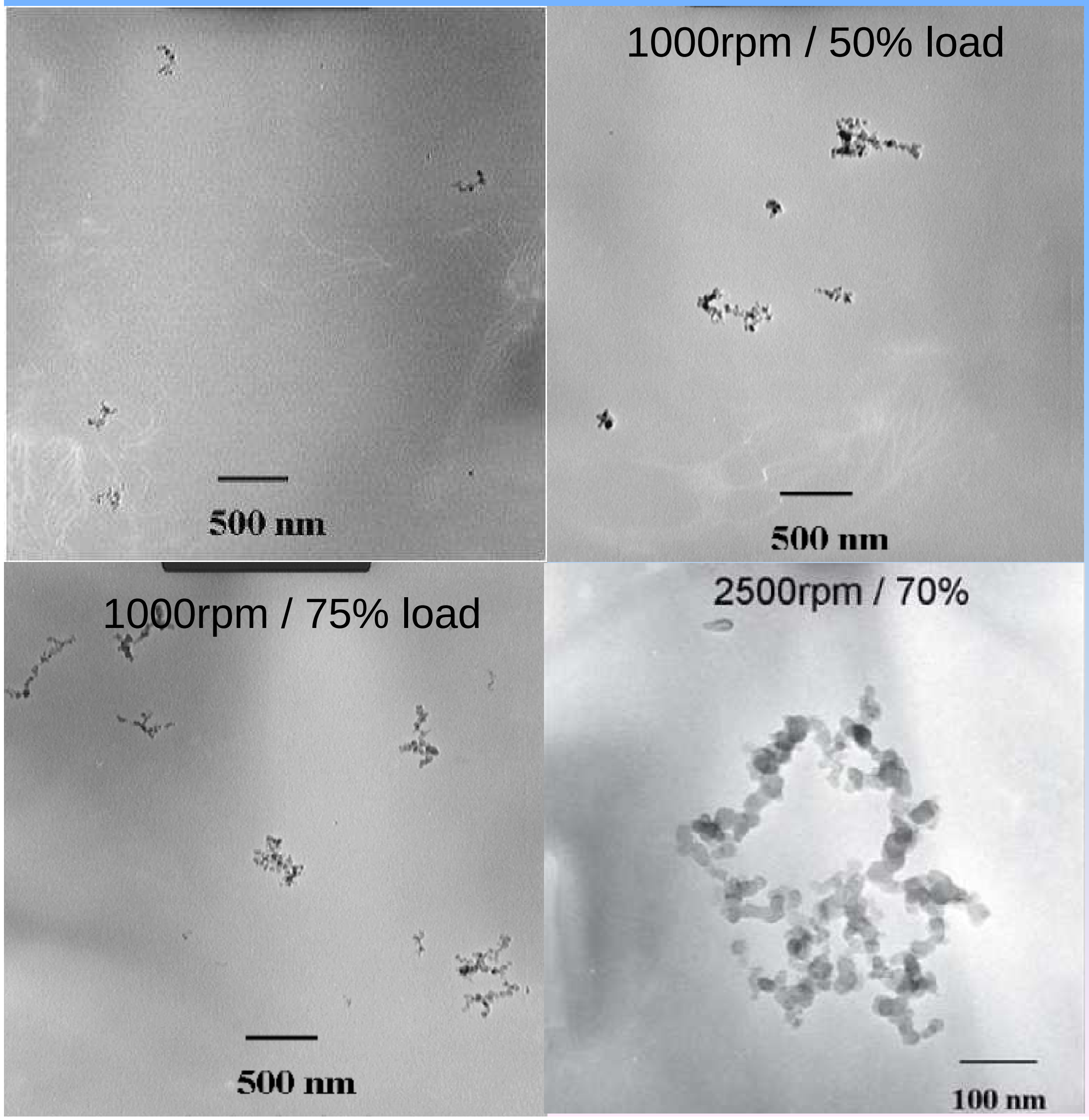
TEM images of nanoparticles sampled from a Diesel exhaust



- soot
- carbon black
- black carbon
- elemental carbon
- **refractory carbon**

"Life exists in the universe only because the carbon atom possesses certain exceptional properties"

James Jeans

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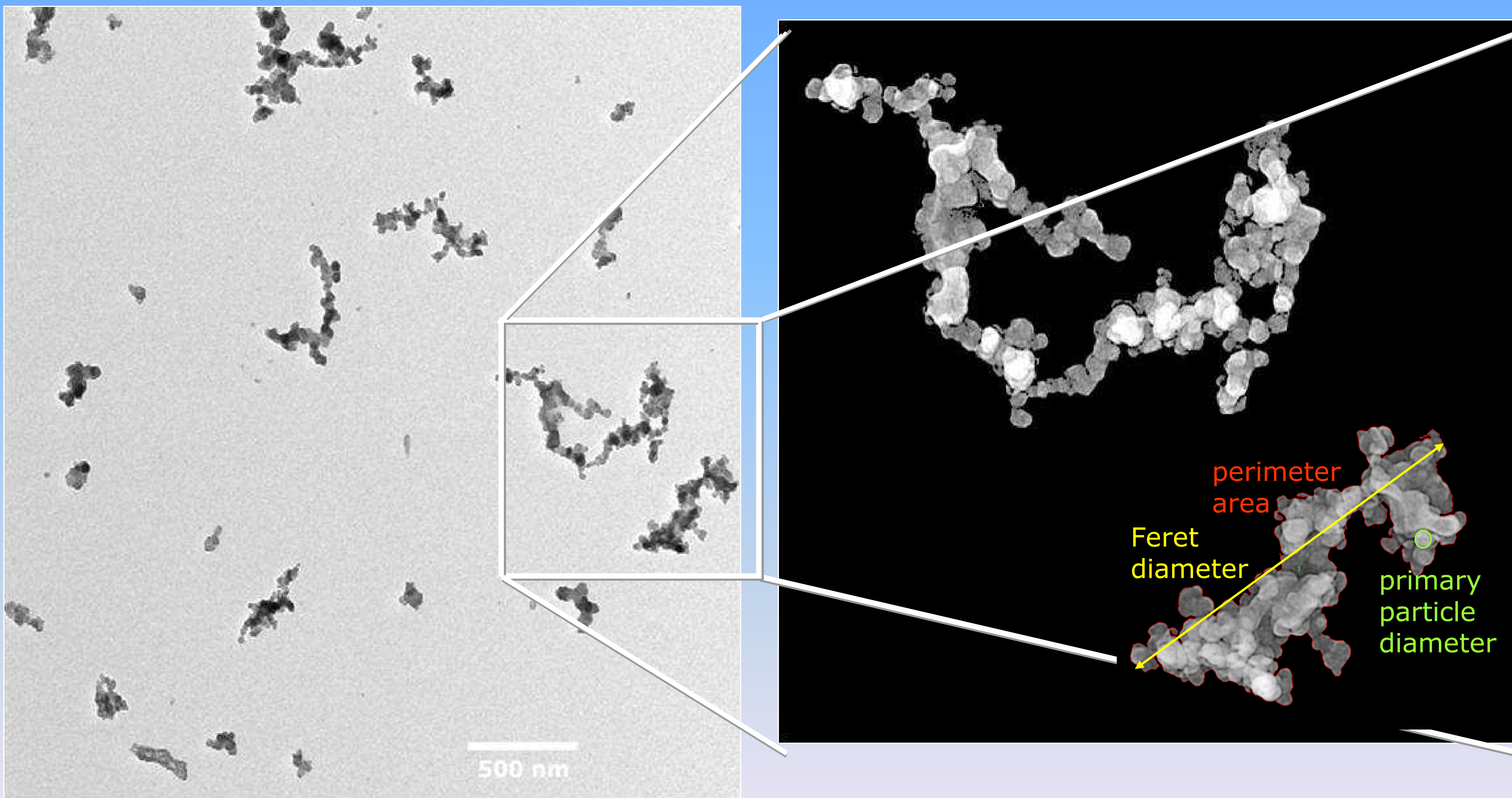
TEM Imaging of Flame Soot



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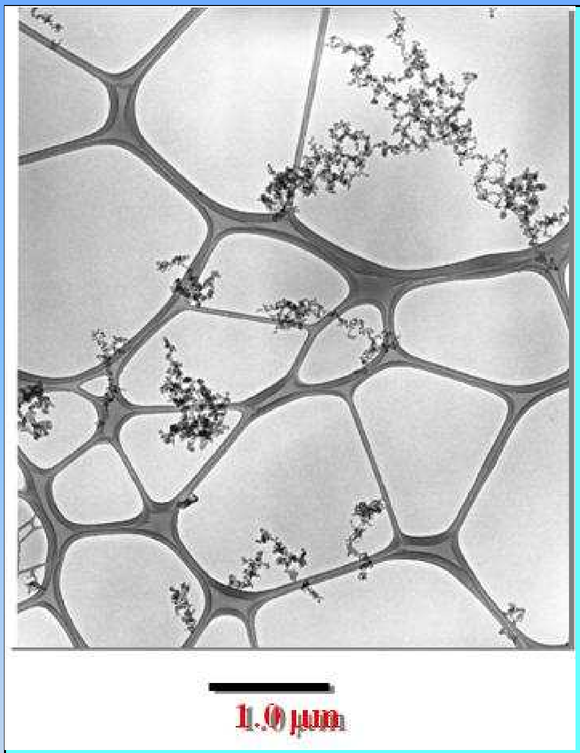
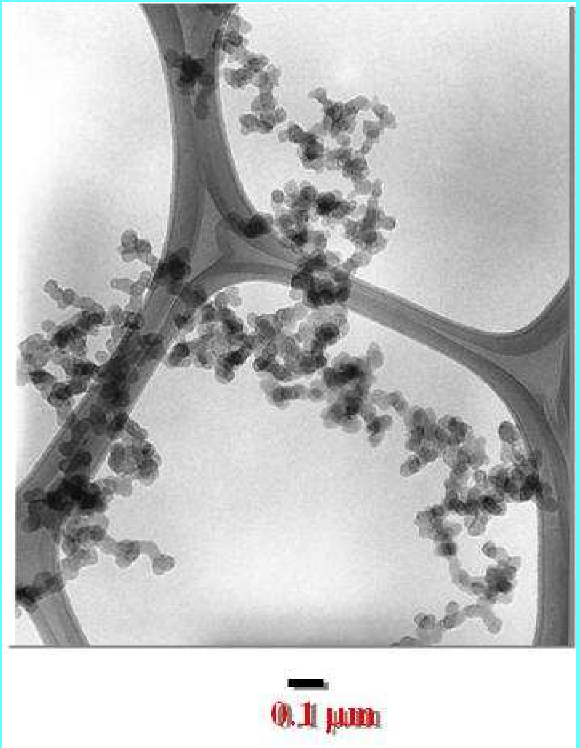
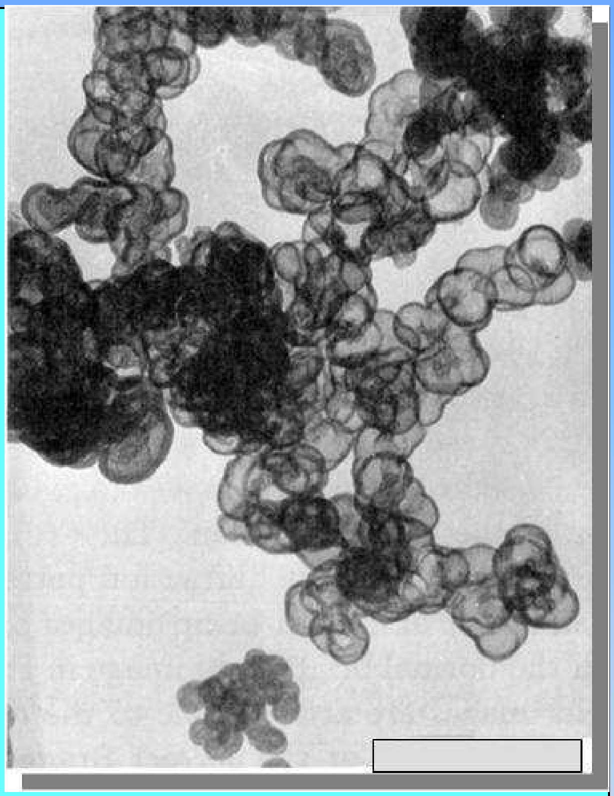
Transmission Electron Microscope (TEM) Images of Soot







Morphology

- nearly-spherical primary particles 20–50 nm in diameter
- SOF absorbed onto the surface of the primary particles
- Primary particles cluster into chain-like aggregates

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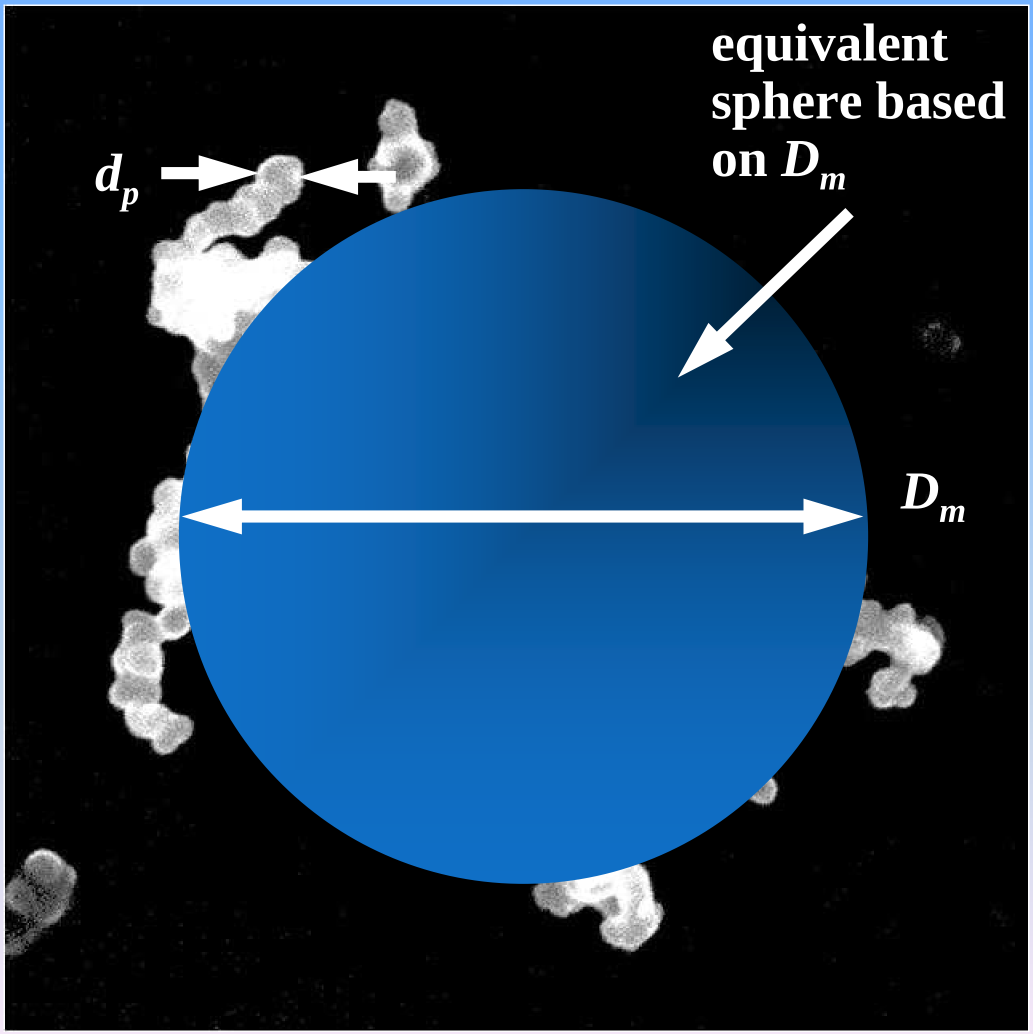
SEM Image of Flame Soot

Others assume an "equivalent sphere diameter", **what's the density?**



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What Does LII Do?

- Quantitative measurement for dry soot:
  - concentration (0.5 ppt – 10 ppm volume; 1μg/m^3 – 20g/m^3 mass)
  - active surface area (50 – 200 m^2/g)
  - primary particle diameter (typically 5-50 nm)
  - number density of primary particles
- Measurement features:
  - very high precision and resolution
  - transient concentration
  - nonintrusive (dilution unnecessary)
  - wide range of applicability
  - potential standardized method
  - measures soot
  - uninfluenced by the presence of other species

Technology Licensed from NRC, Canada

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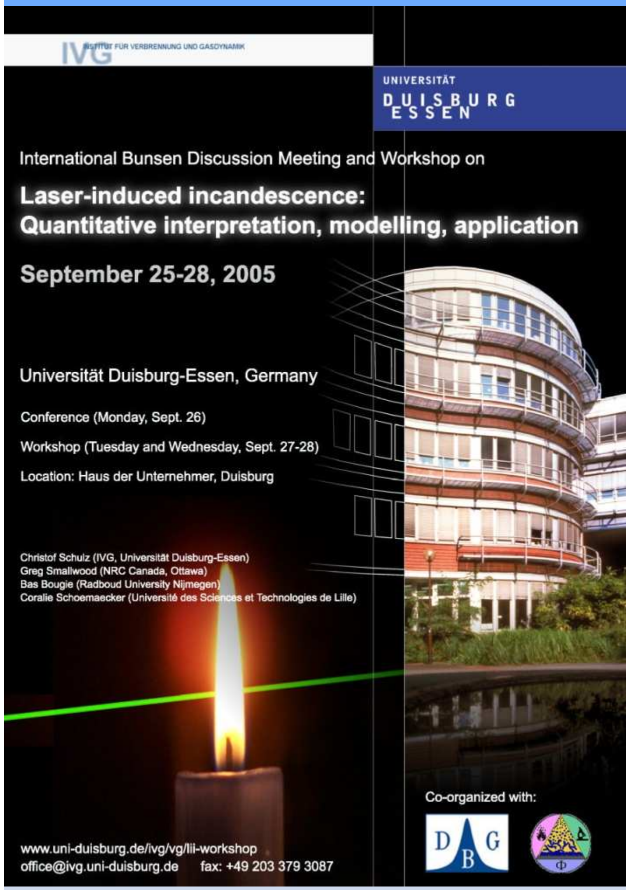
NRC Canada LII Innovations

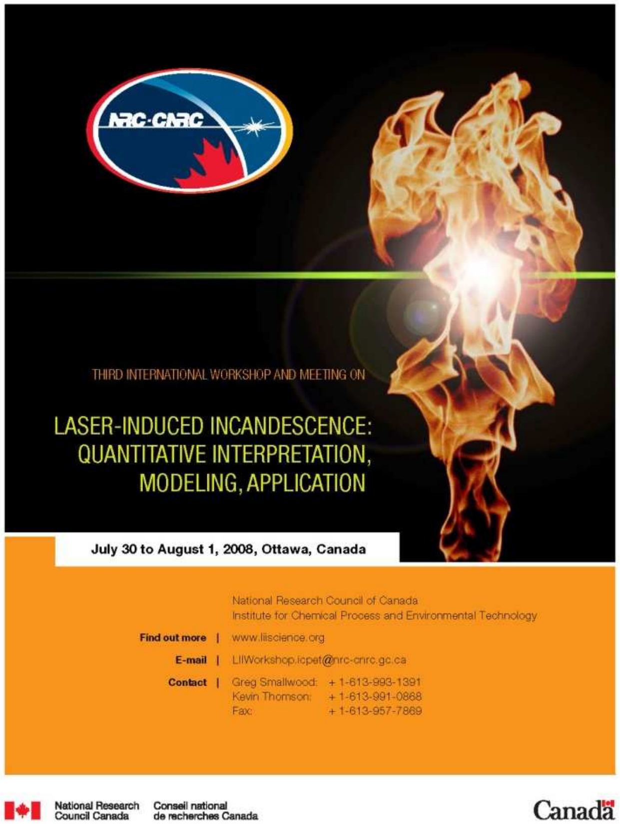
- Absolute intensity (patented)
  - spectral radiance calibration
- Real-time two-color pyrometry (patented)
  - particle temperature
- Laser beam profile (patented)
  - uniform heating
- Low laser fluence (patented)
  - no sublimation

Science Behind LII



2005

2006



2008

Next Meeting: **4th International Discussion Meeting and Workshop**
Laser-Induced Incandescence: Quantitative Interpretation, Modeling, Application
April 18 – 20, 2010, Varenna, Italy

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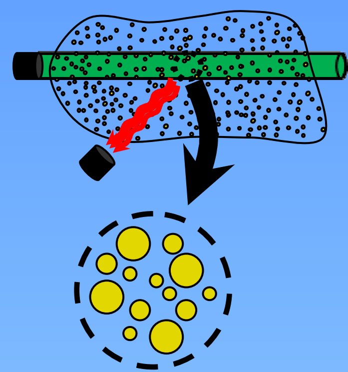
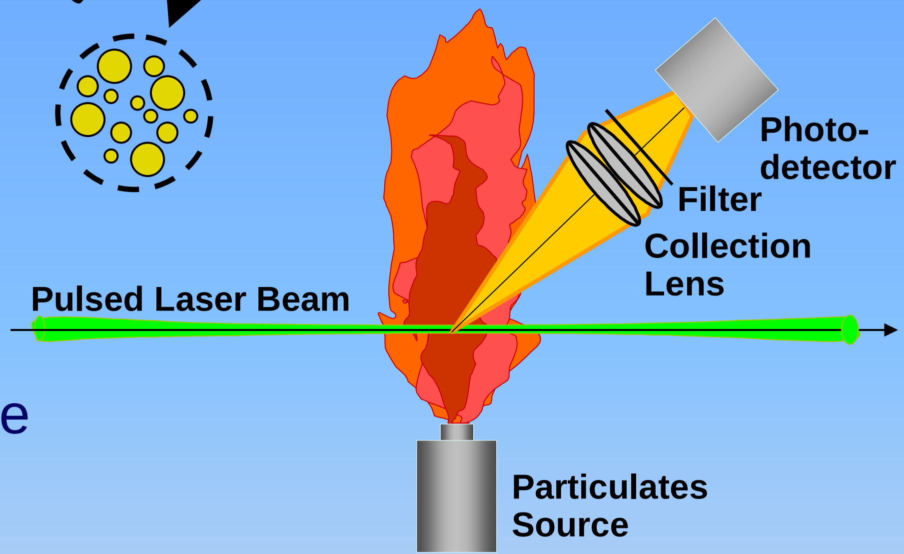
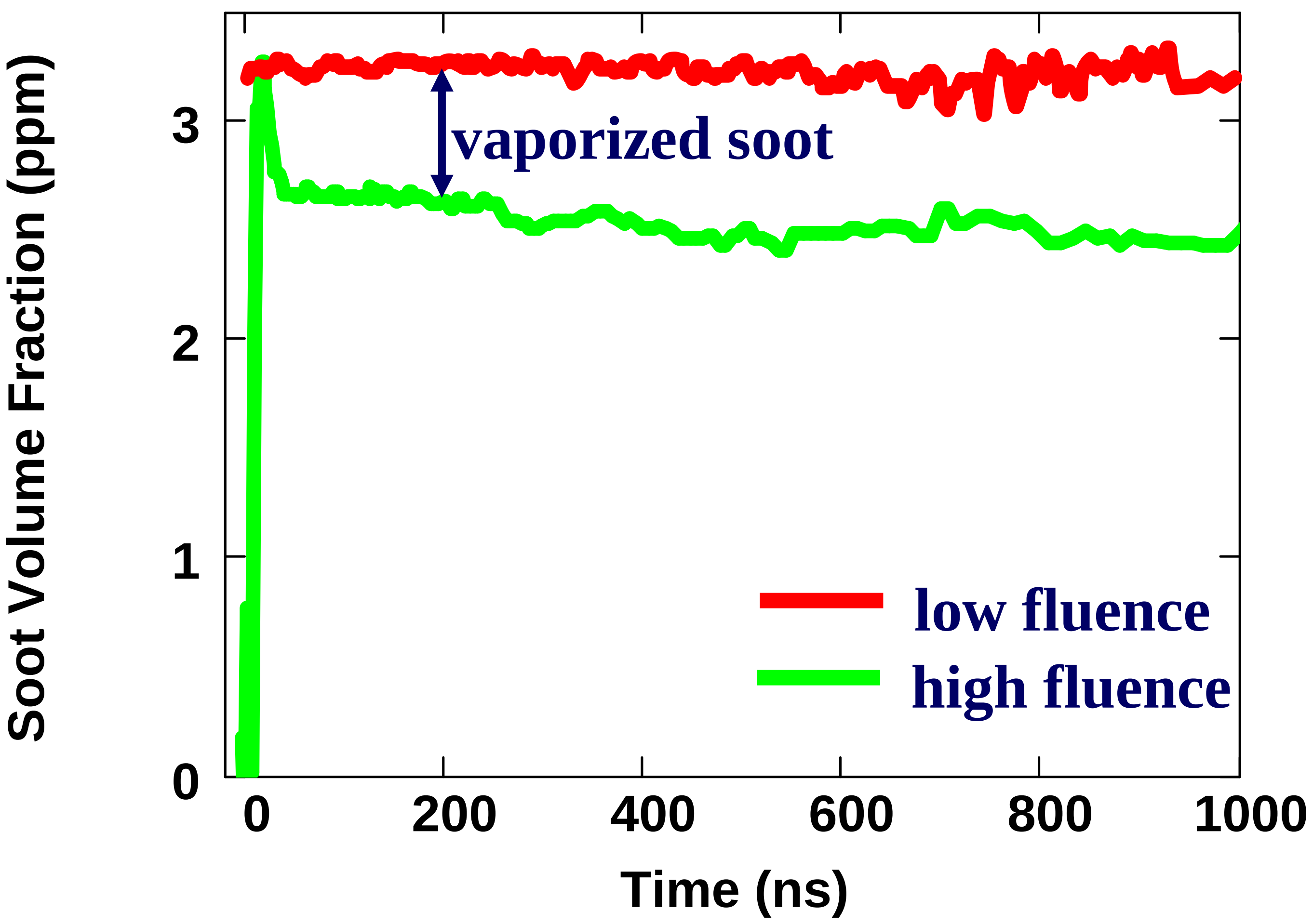
LII Concepts





- **LII experiment**:
  - pulsed laser beam
  - rapid heating of soot to evaporation temperature
  - soot radiates incandescence as it cools to ambient temperature
  - incandescence signal is collected to determine soot concentration, surface area, and primary particle diameter
- **LII theory**
  - a state-of-the-art numerical model of nanoscale (time and space) heat transfer to and from the particles

Soot Volume Fraction – Fluence Effects



Auto-Compensating LII (AC-LII)

- **Two-color pyrometry** coupled with LII to determine the time-resolved particle temperature
  - permits use of low-fluence
  - particles are kept below the sublimation temperature
- This new technique ***automatically compensates*** for any changes in the experimental conditions
  - fluctuations in local ambient temperature
  - variation in laser fluence
  - laser beam attenuation by the particulate matter
  - desorption of condensed volatile material

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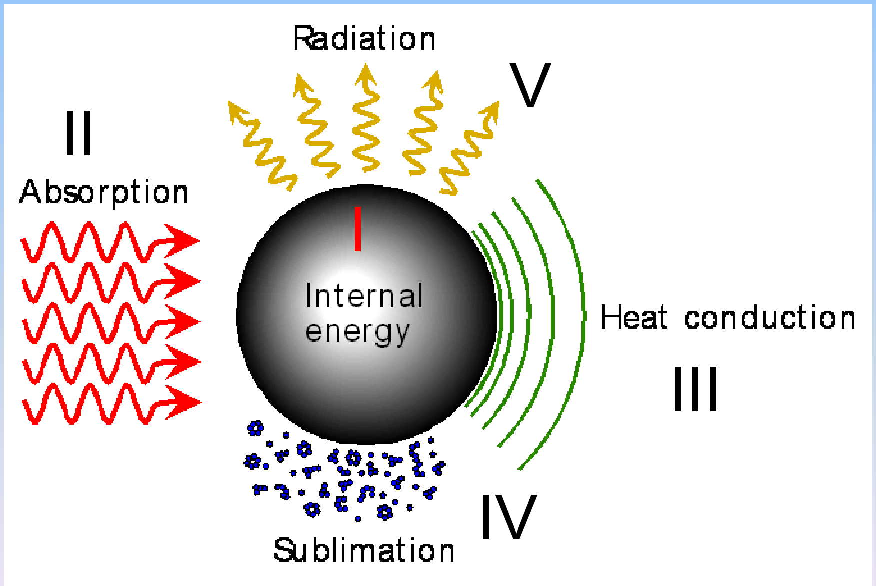
Soot Particle Heat Transfer Equation

$$\underbrace{\frac{\pi D^3}{6}\rho_s c_s \frac{dT}{dt}}_{\mathrm{I}} = \underbrace{C_a q}_{\mathrm{II}} - \underbrace{\frac{2 k_a (T - T_0)\pi D^2}{(D + G\lambda_{MFP})}}_{\mathrm{III}} + \underbrace{\frac{H_v}{M_v}\frac{dM}{dt}}_{\mathrm{IV}} - \underbrace{q_{rad}}_{\mathrm{V}}$$



[Michelsen *et al.*, Third International Discussion Meeting and Workshop on Laser-induced incandescence: Quantitative interpretation, modelling, application, 2008]

- I change in internal energy
- II laser heating
- III heat transfer to surrounding gas
- IV soot sublimation
- V radiative heat loss

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Particulate Concentration

- Determine calibration factor

$$\eta(\lambda) = \frac{V_{CAL}(\lambda)}{R_S(\lambda, T)}$$

- Measure incandescence, $P_p(\lambda)$, at two wavelengths and solve for temperature, T

$$\frac{P_p(\lambda_1)}{P_p(\lambda_2)} = \frac{\lambda_2{}^6}{\lambda_1{}^6} \frac{\left(e^{\frac{hc}{k\lambda_2 T}} - 1\right)}{\left(e^{\frac{hc}{k\lambda_1 T}} - 1\right)} \frac{E(m_{\lambda_1})}{E(m_{\lambda_2})}$$

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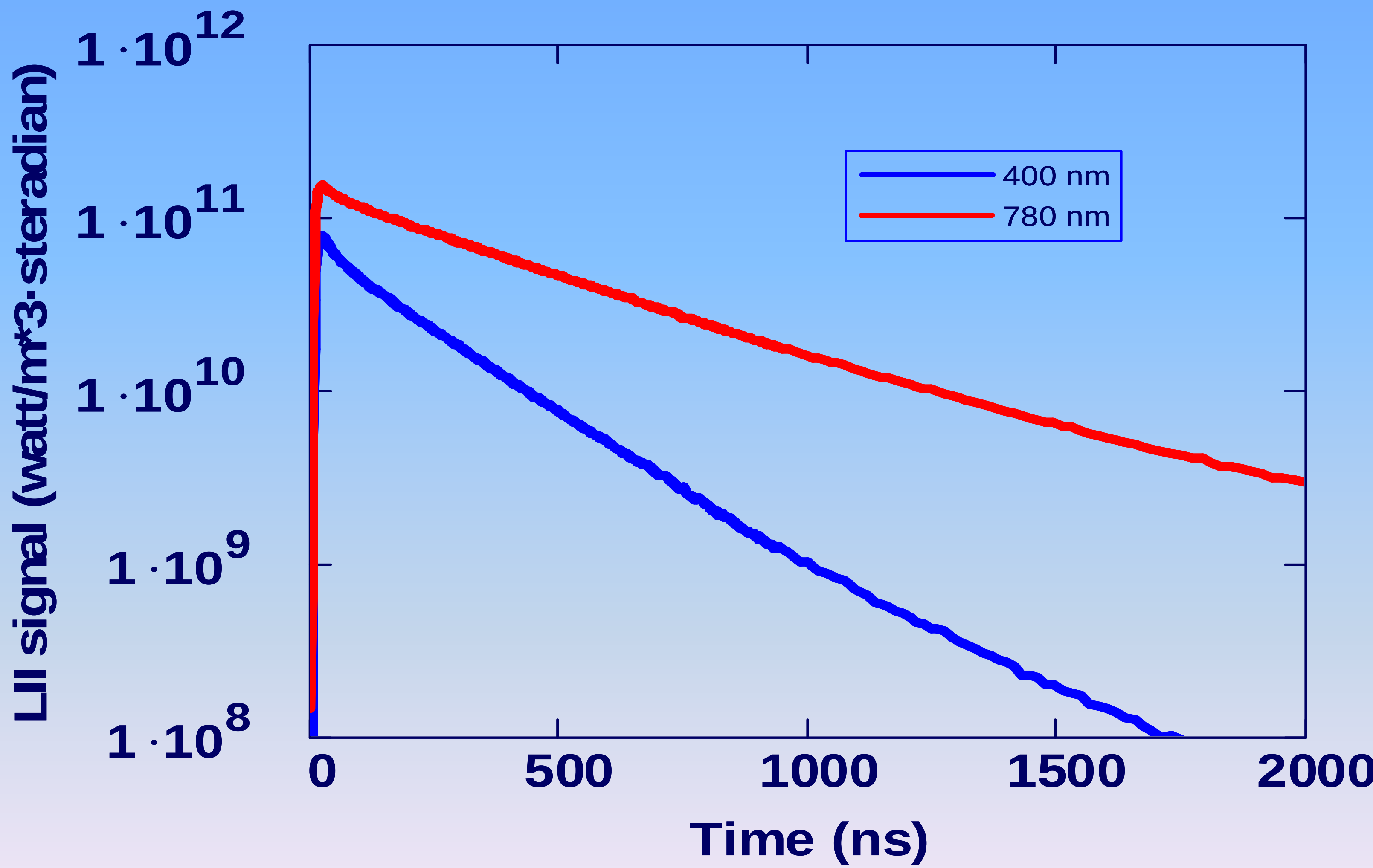
Absolute LII Signals



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Two-Color Pyrometry

- relative signal at two wavelengths:

$$\frac{V_{EXP}(\lambda_1)}{V_{EXP}(\lambda_2)} = \frac{\eta(\lambda_1)}{\eta(\lambda_2)} \cdot \frac{\lambda_2{}^6}{\lambda_1{}^6} \cdot \frac{\left(e^{\frac{hc}{k\lambda_2 T}} - 1\right)}{\left(e^{\frac{hc}{k\lambda_1 T}} - 1\right)} \frac{E(m_{\lambda_1})}{E(m_{\lambda_2})}$$

- where:
  - V_{EXP} is the LII measured signal (volts)
  - λ_1 and λ_2 are the detection wavelengths for each channel
  - $\eta(\lambda)$ is the calibration factor (relating measured volts to the source radiance)
  - *h*, *c*, and *k* are the Planck constant, speed of light, and Boltzmann constant, respectively
  - *T* is the temperature (K)
  - *E*(*m*) is the absorption function, an optical property of soot
- the equation is solved to determine temperature

$$T = \frac{hc}{k}\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)\left[\ln\left(\frac{V_{\exp_1}\lambda_1{}^6}{\eta_1 E(m_{\lambda_1})}\right) - \ln\left(\frac{V_{\exp_2}\lambda_2{}^6}{\eta_2 E(m_{\lambda_2})}\right)\right]$$

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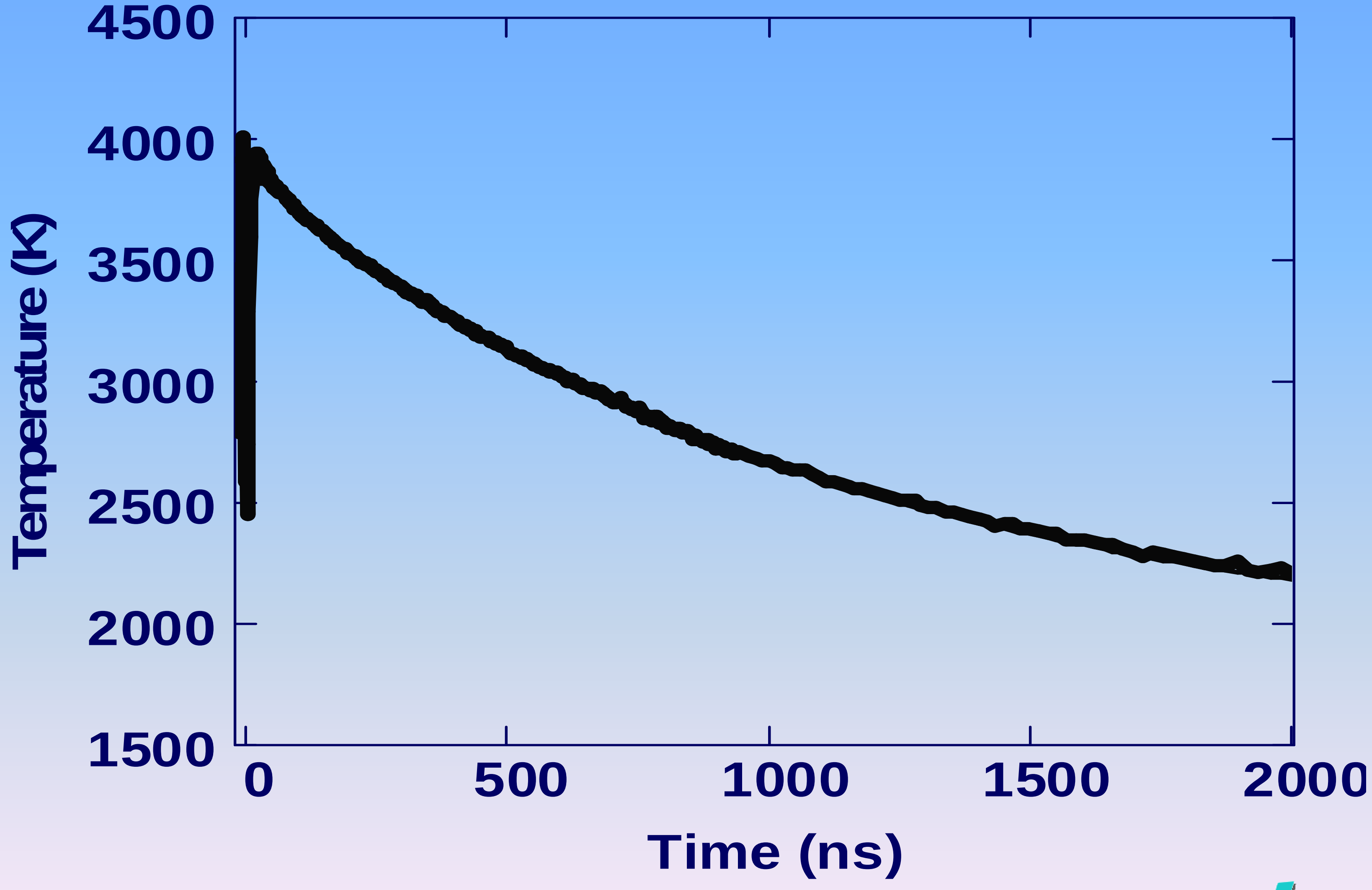
Real-Time Temperature



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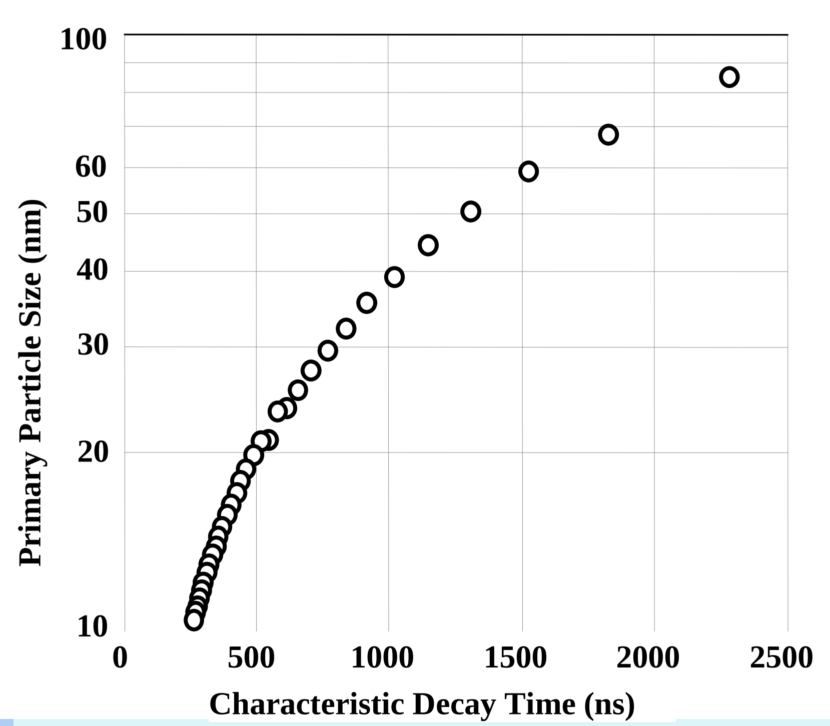
Primary Particle Size

- The temperature differential between the particle surface and the ambient gas decays steadily in an exponential manner

$$T - T_g = A \cdot e^{-\Delta t \tau}$$

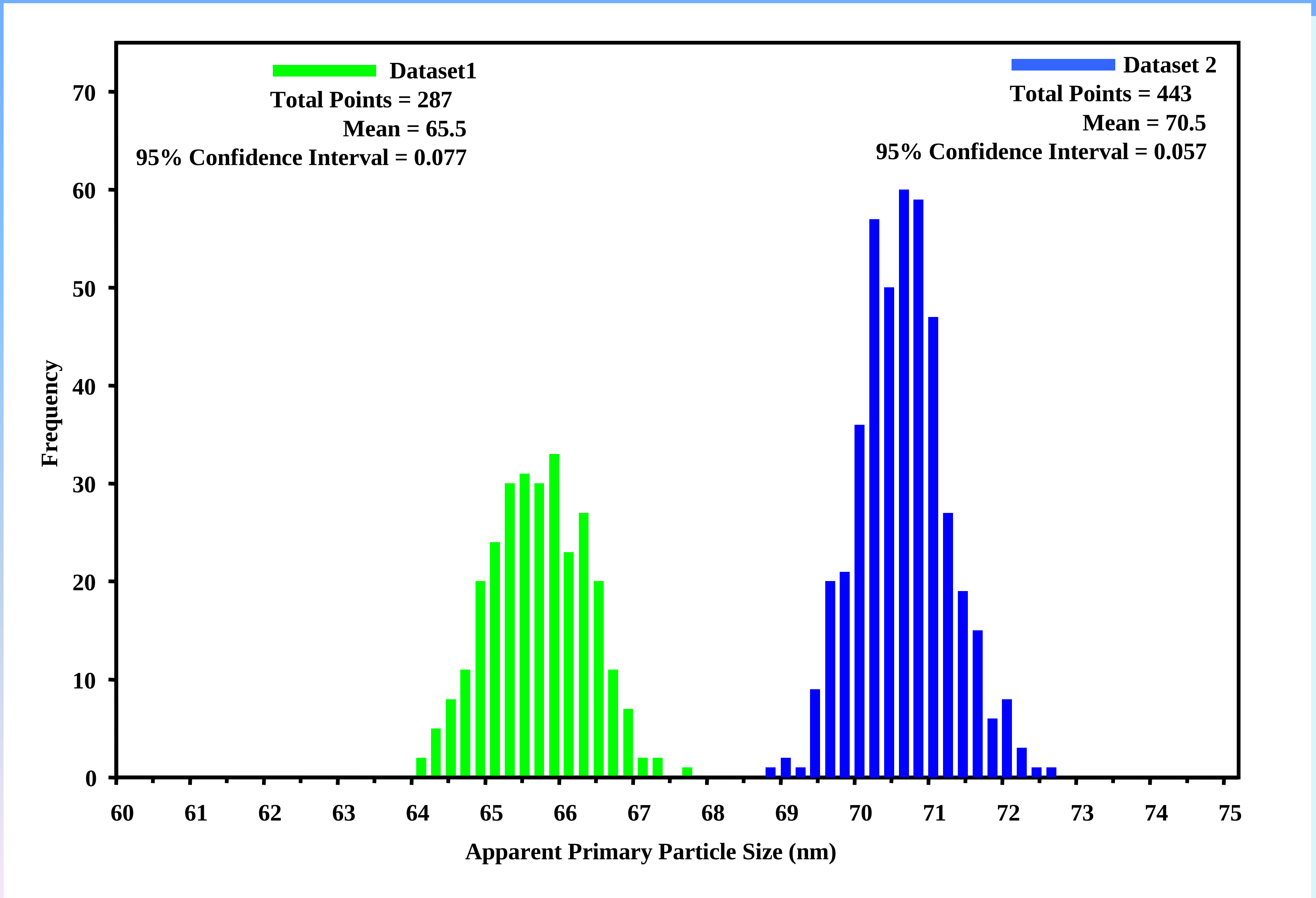


- The primary particle diameter may be inferred *(McCoy and Cha, 1974)*

$$d_p = \frac{12 k_g \alpha}{G \lambda_{MFP} c_p \rho_p \tau}$$

Characteristic decay time

Soot primary Particle Size at Two Combustion Conditions
Carbon Black Production



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Primary Particle Size: Discussion

- the number of primary particles is also determined
- primary particle size can also be used to determine active surface area
- aggregate size is of greater interest from the health, environment, and regulation perspectives
- knowledge of primary particle size and number provides insight about aggregate morphology

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Particulate Concentration

- **Particle (soot) volume fraction is known to be**

$$f_v = n_p \cdot \frac{\pi d_p^3}{6}$$

- **Combining the above equation with the calibration factor and the particle leads to**

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Soot Volume Fraction

- soot volume fraction:

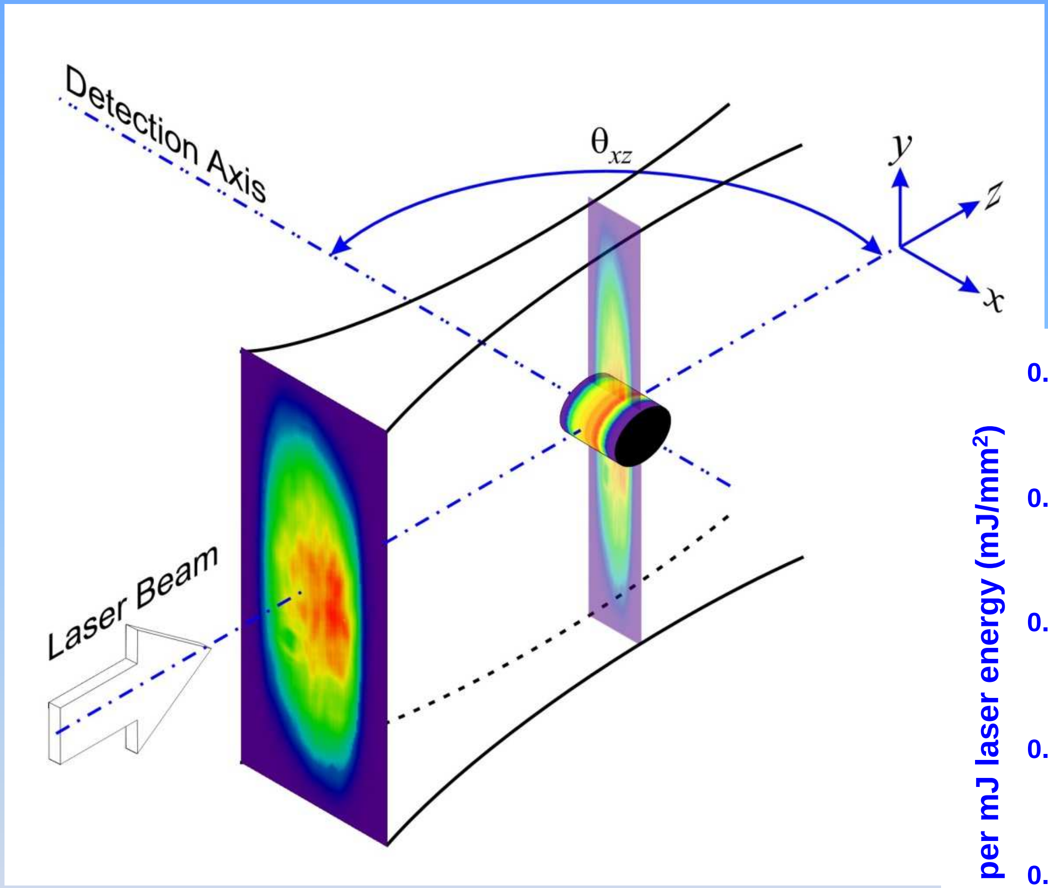
$$f_v = \frac{V_{EXP}(\lambda)}{\eta(\lambda)\, w_b} \frac{\lambda^6 \left(e^{\frac{hc}{k\lambda T}} - 1 \right)}{12\pi c^2 h\, E(m_\lambda)}$$

- where:
  - w_b is the laser sheet width, which determines the depth of the measurement volume
  - the other parameters are the same as described previously
- the area of the measurement volume is the same as the area observed with the calibration lamp, and all the optics and electronics (filters, lenses, photomultipliers, amplifiers, etc.) are the same for the calibration and the LII measurement
- note that the soot volume fraction is inversely proportional to $E(m)$, the soot absorption function

What Do We Need to Know in Advance?

- calibration source
  - spectral radiance
- optics
  - absolute optical filter transmission
  - relative dichroic mirror reflectivity
  - relative interference filter transmission
- electronics
  - relative photodetector sensitivity
  - photodetector gain
  - amplifier gain
- dimensions of probe volume
- laser spatial fluence profile

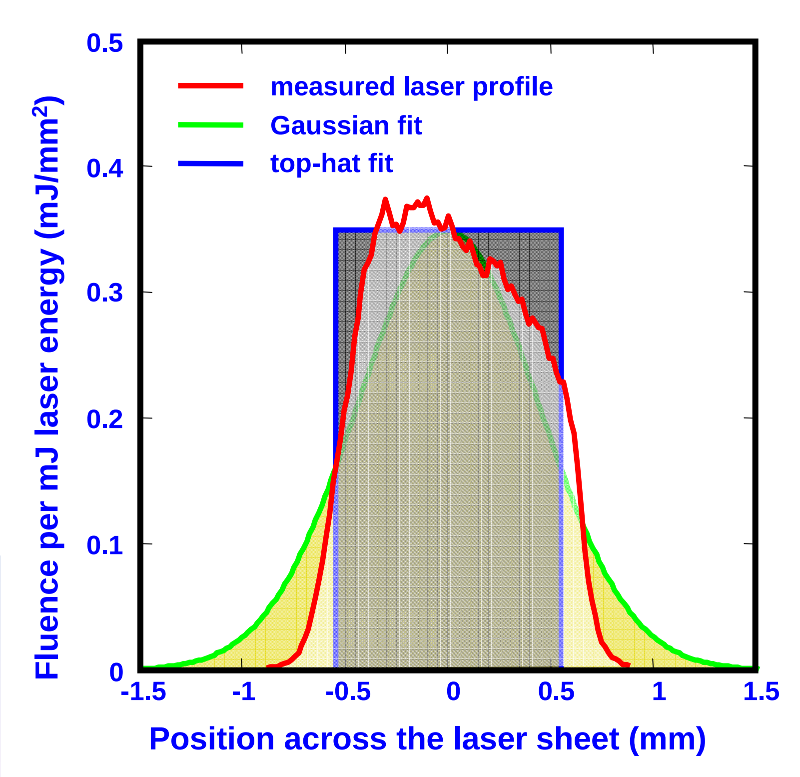
Laser Light Beam Spatial Profile



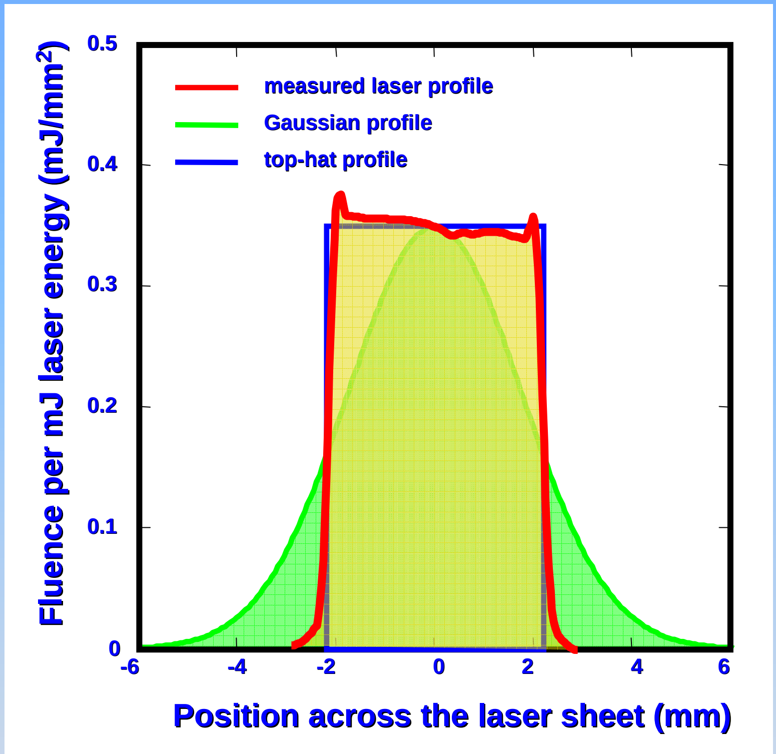
- each fluence level will heat particles to a different temperature
- ideal is a top-hat profile

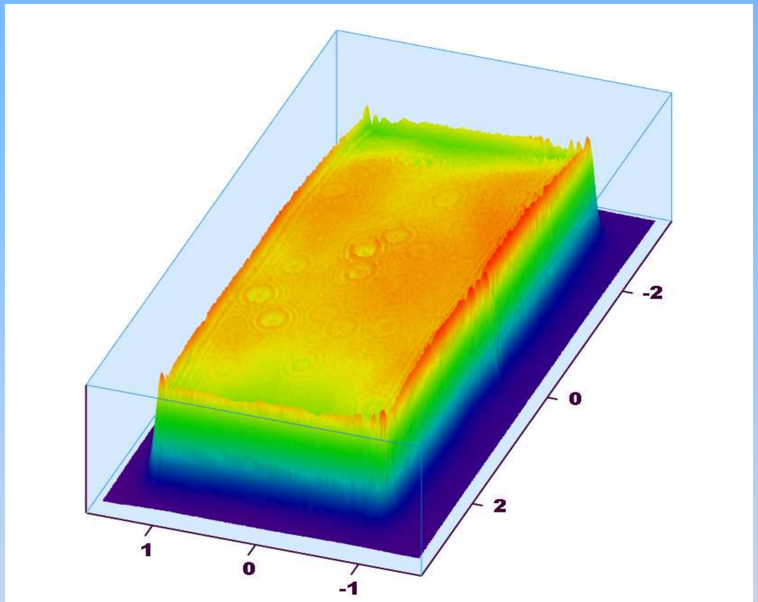
⇑ Gaussian sheet

multimode “tophat” ⇒



Relay Imaging for Top Hat Profile





- place rectangular aperture in laser beam
- relay image aperture to probe volume location

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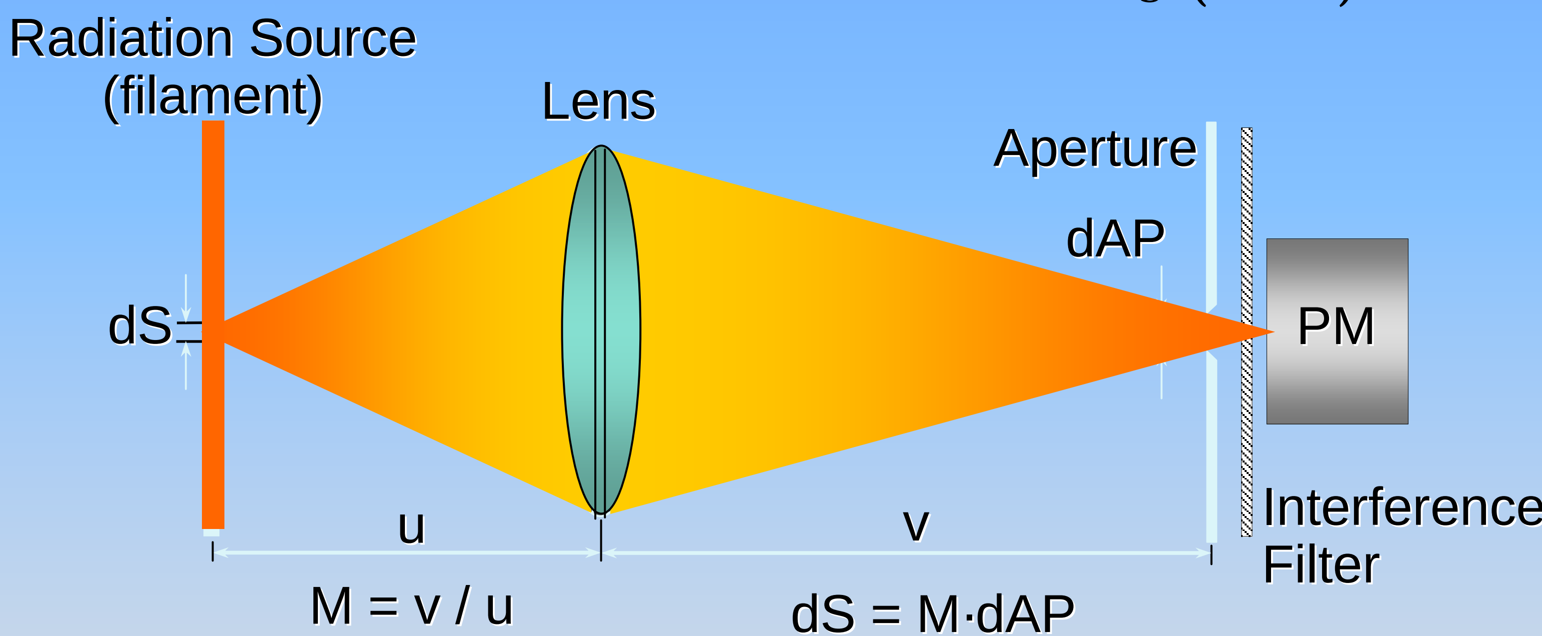
Absolute Intensity Calibration

Calibration Factor

$$\eta(\lambda) = \frac{V_{CAL}(\lambda)}{R_S(\lambda, T)}$$



- use two-color pyrometry to determine the filament temperature
- use known filament radiant power incident on the aperture to calibrate the detection system (NIST-traceable spectral radiance calibration)

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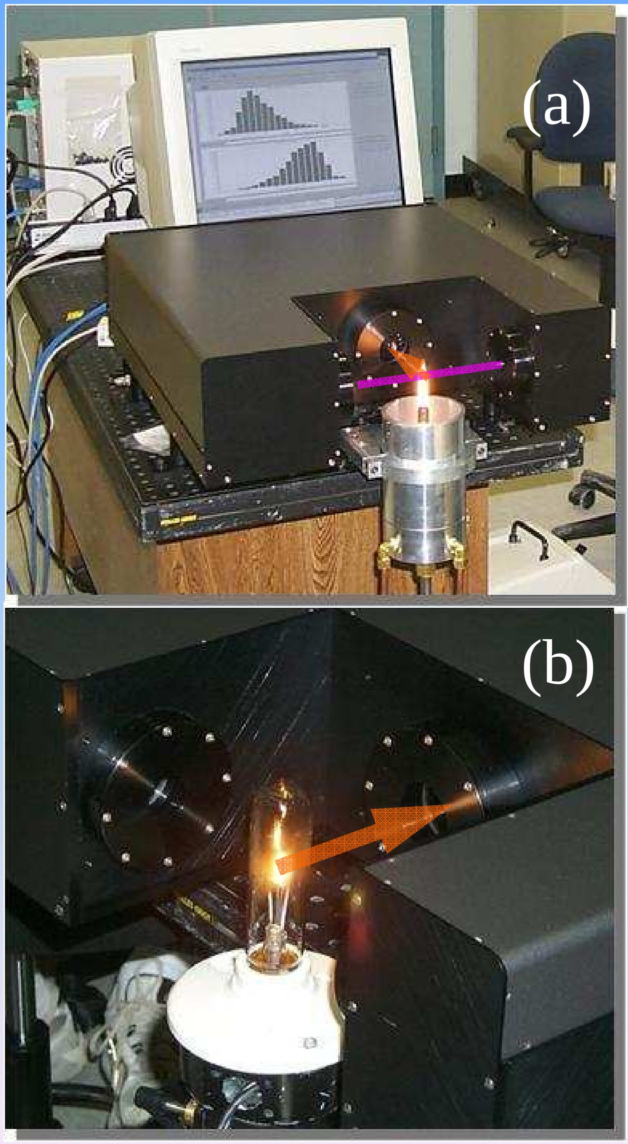
Artium Technologies LII 200 Instrument

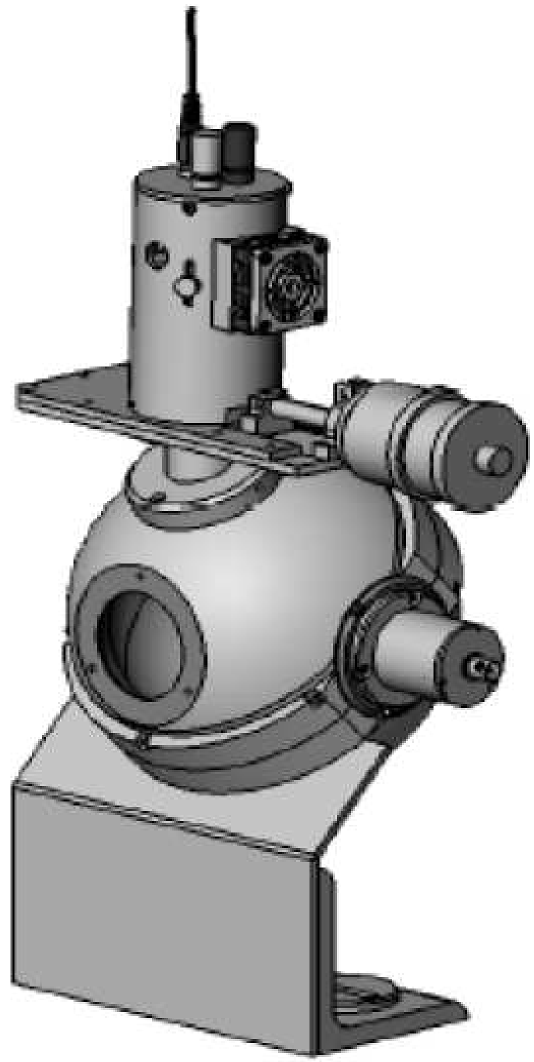


a) Soot source in measurement volume (sampling cell removed to aid illustration)
b) Lamp replacing soot as source of incandescence

- NIST – traceable calibration procedure
  - lamp is a calibrated spectral radiance source, in Watts/m^3-steradian
  - tungsten strip filament lamp is used
  - photomultiplier signal is recorded for a number of calibrated filament temperatures to ensure accurate calibration
  - a single calibration factor, $\eta(\lambda)$, is determined for each wavelength channel (400 nm and 780 nm)
  - electronic gain of photomultipliers (PM) are independently calibrated for different PM bias voltages

Luminance / Radiance Standards

- Traceable Luminance & Radiance Standards
- <1" to >24" Port Sizes
- Low-Light Level Calibration (Night Vision)
- CCT/Spectral Monitoring
- Variable Output Levels
- Custom Solution Designs



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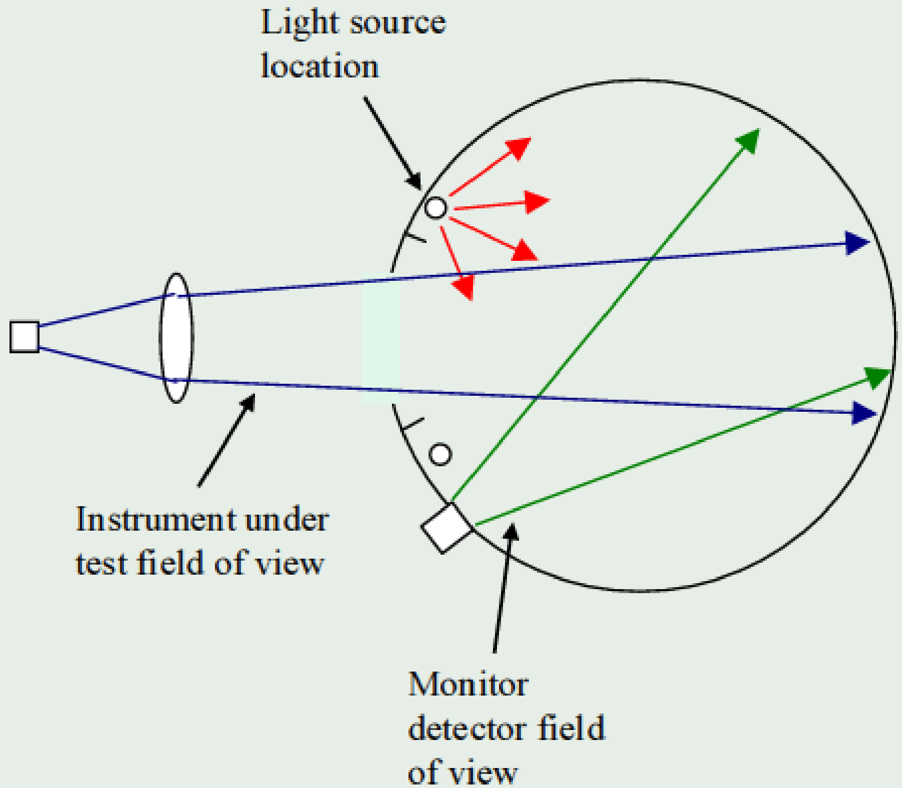
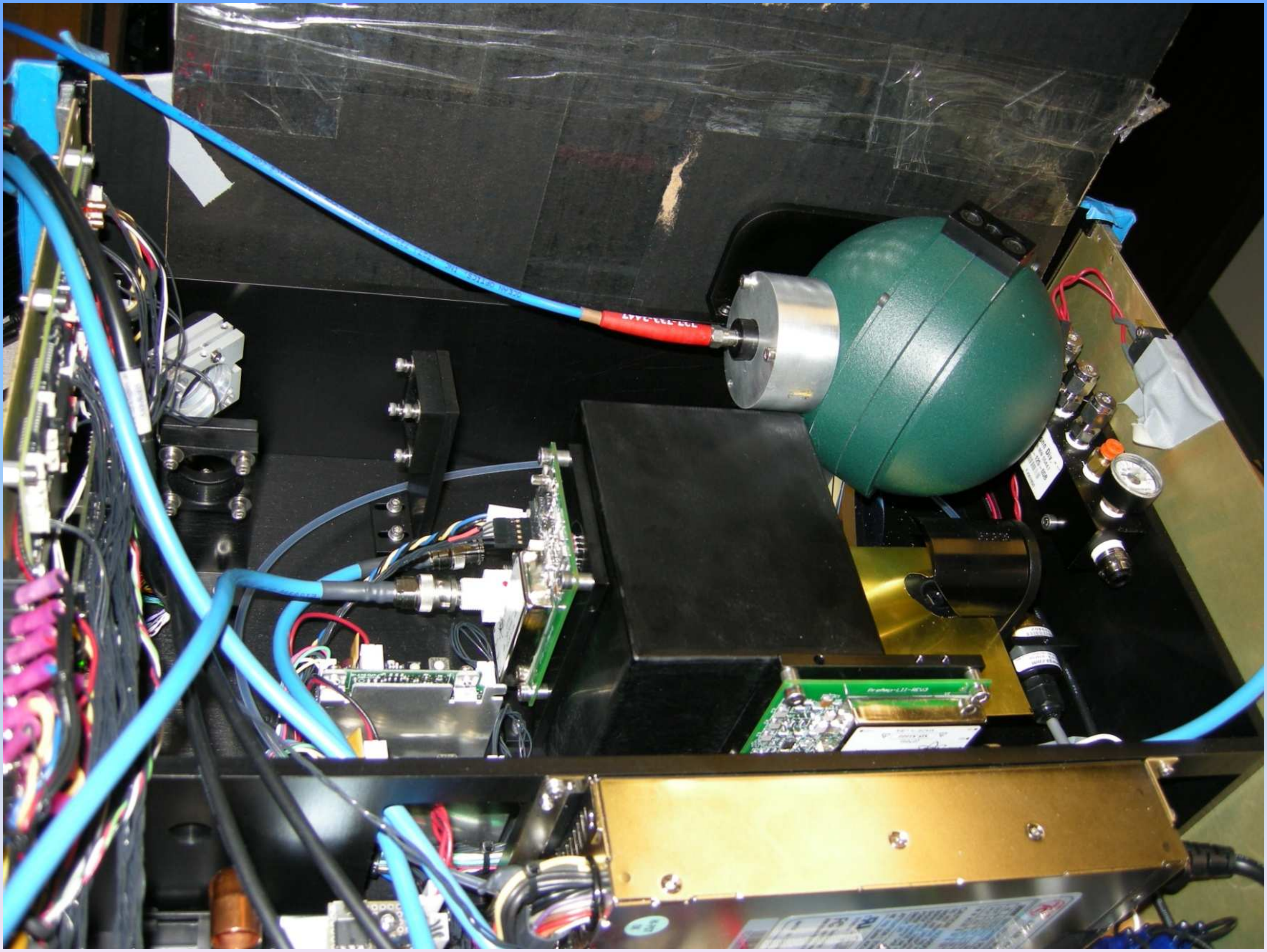
Radiance Standard Anatomy



Sphere Radiance $\boxed{= \dfrac{\phi_i}{\pi A_s} * \dfrac{\rho_0}{1 - \overline{\rho}}}$

Calibration with Integrating Sphere/Spectrometer



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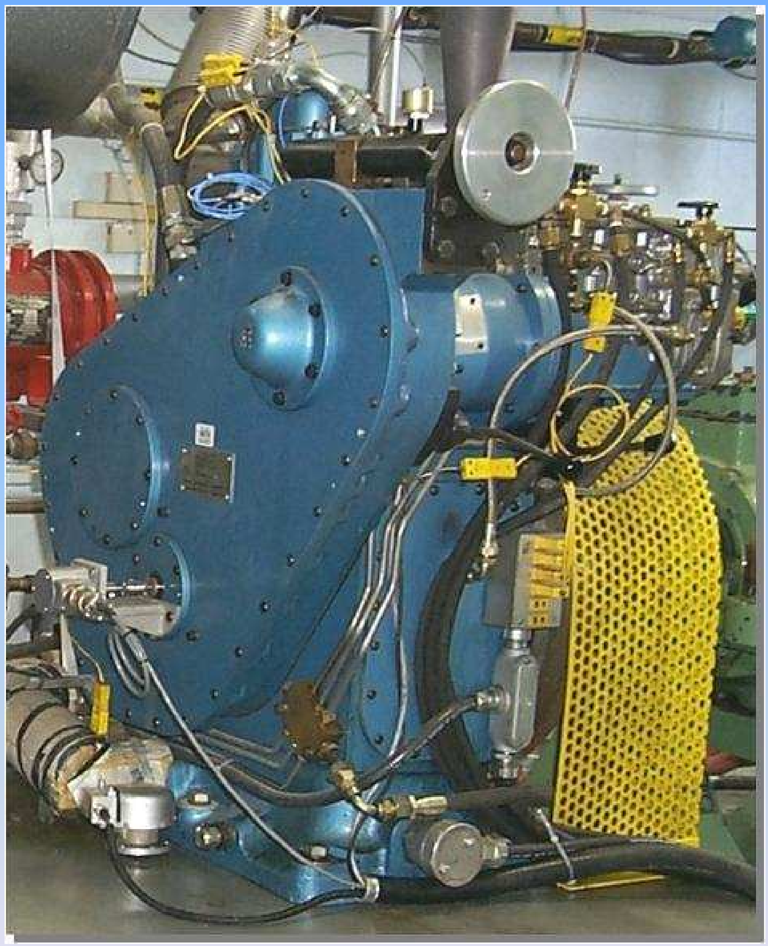
LII TESTING AND VALIDATION

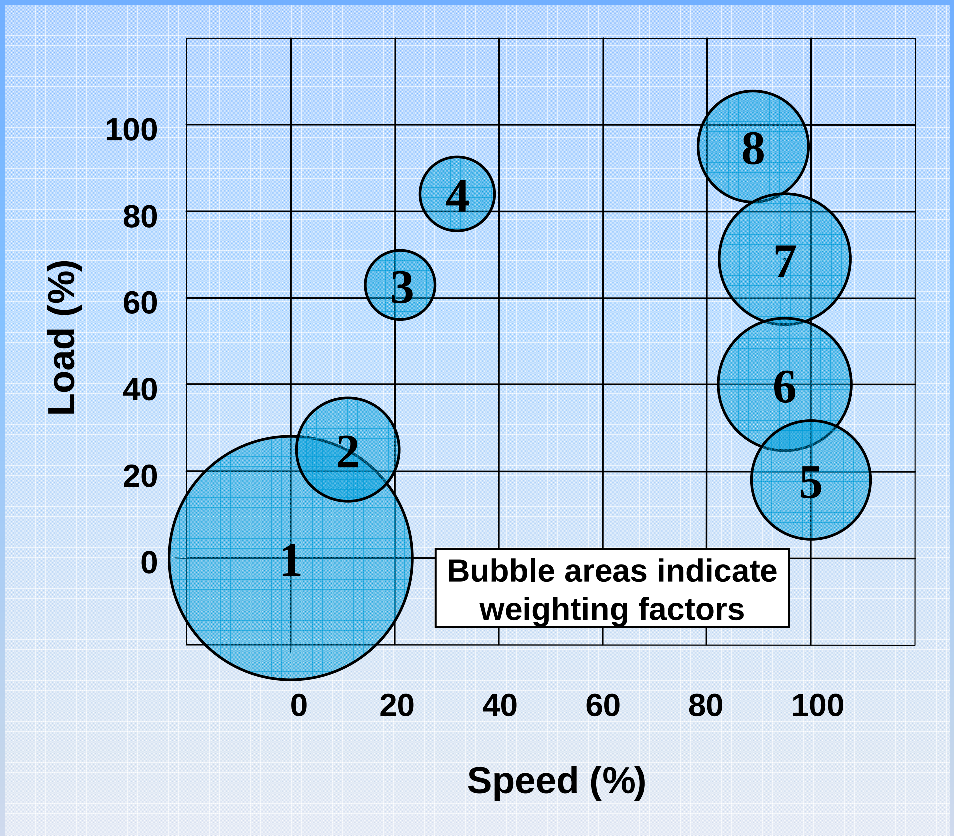
Testing Includes:

- Laboratory diesel engines
- HD Diesels on dynamometers
- On road testing of HD and LD Diesel emissions
- Turbine engine emissions

•Comparisons to Gravimetric and other optical and filter based methods

Applications – Engine dyno measurements

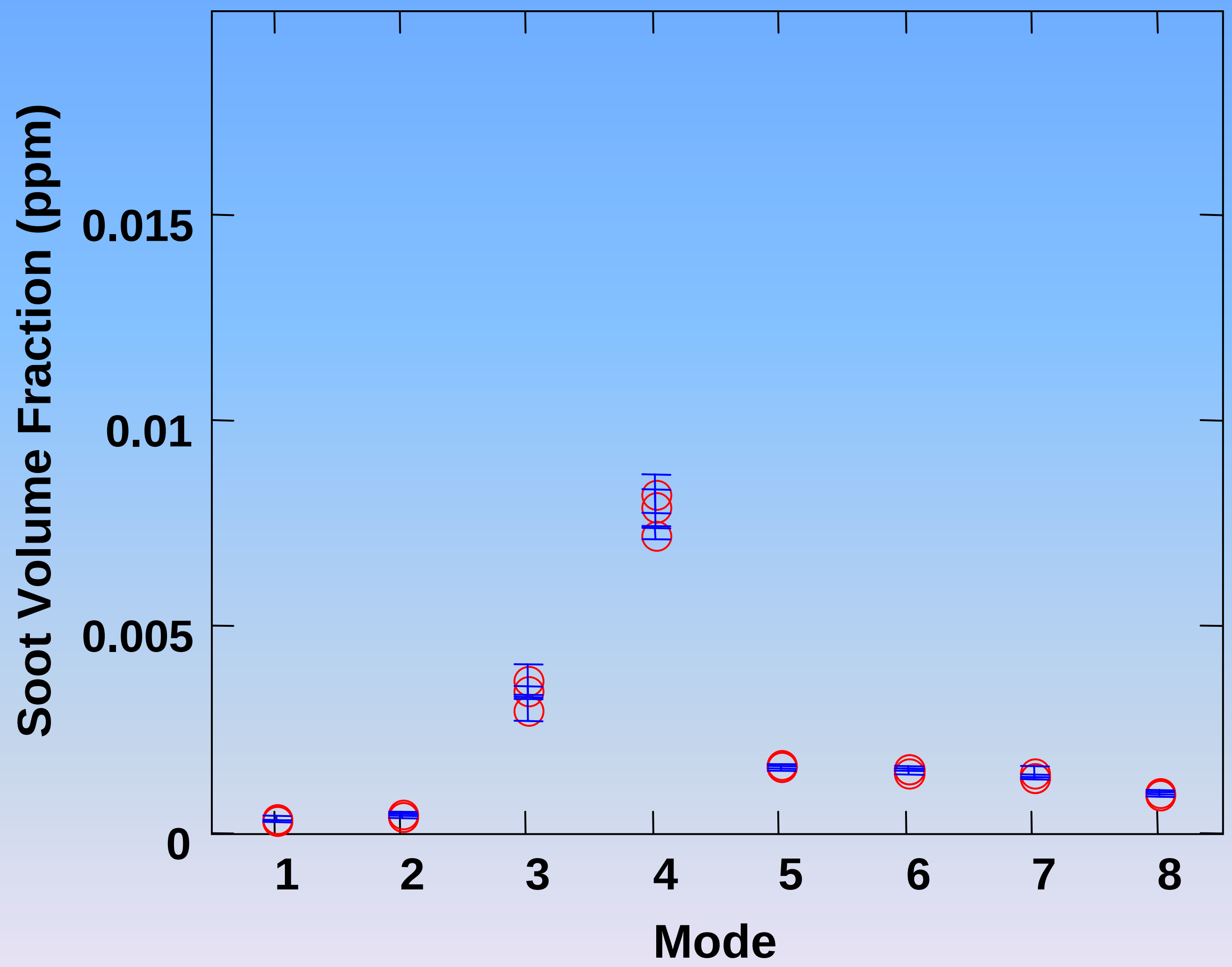




Ricardo Heavy Duty Diesel Engine

AVL 8-Mode Steady-State Simulation

HD Diesel Soot Concentration



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Single Cylinder Heavy-Duty Diesel Engine

Caterpillar 3401E

(NRC Prototype 2004)

Cylinders	1
Volume	2.44 liters
Comp. Ratio	16.25:1
Peak Power (@1800 rpm)	74.6 kW
Valves	4
Injection	EUI
EGR	Cooled

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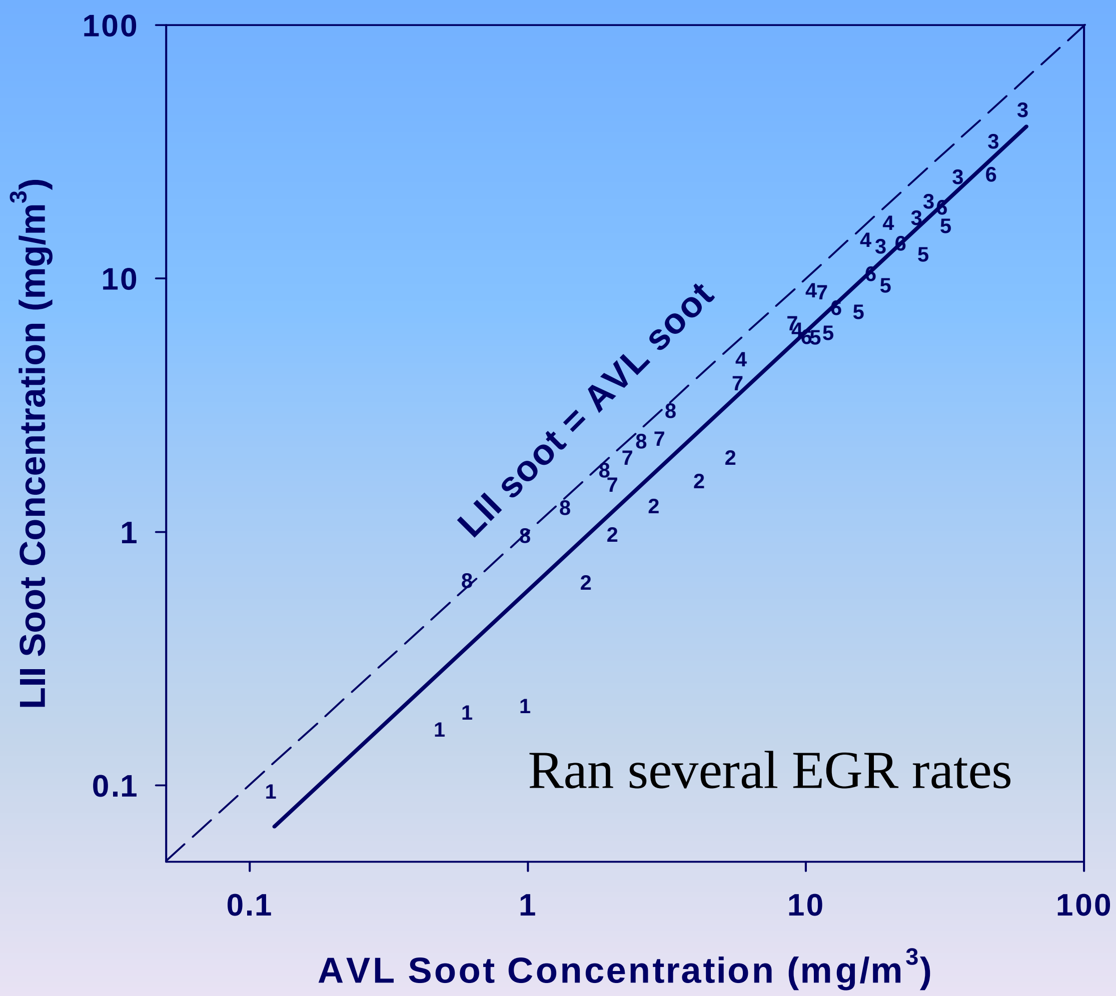
Diesel PM: Soot Concentration



- LII and AVL **Smoke Meter** correlate well over a wide range of engine conditions
- more than two orders of magnitude variation in concentration
- evidence suggests that SOF plays a role, particularly at mode 1

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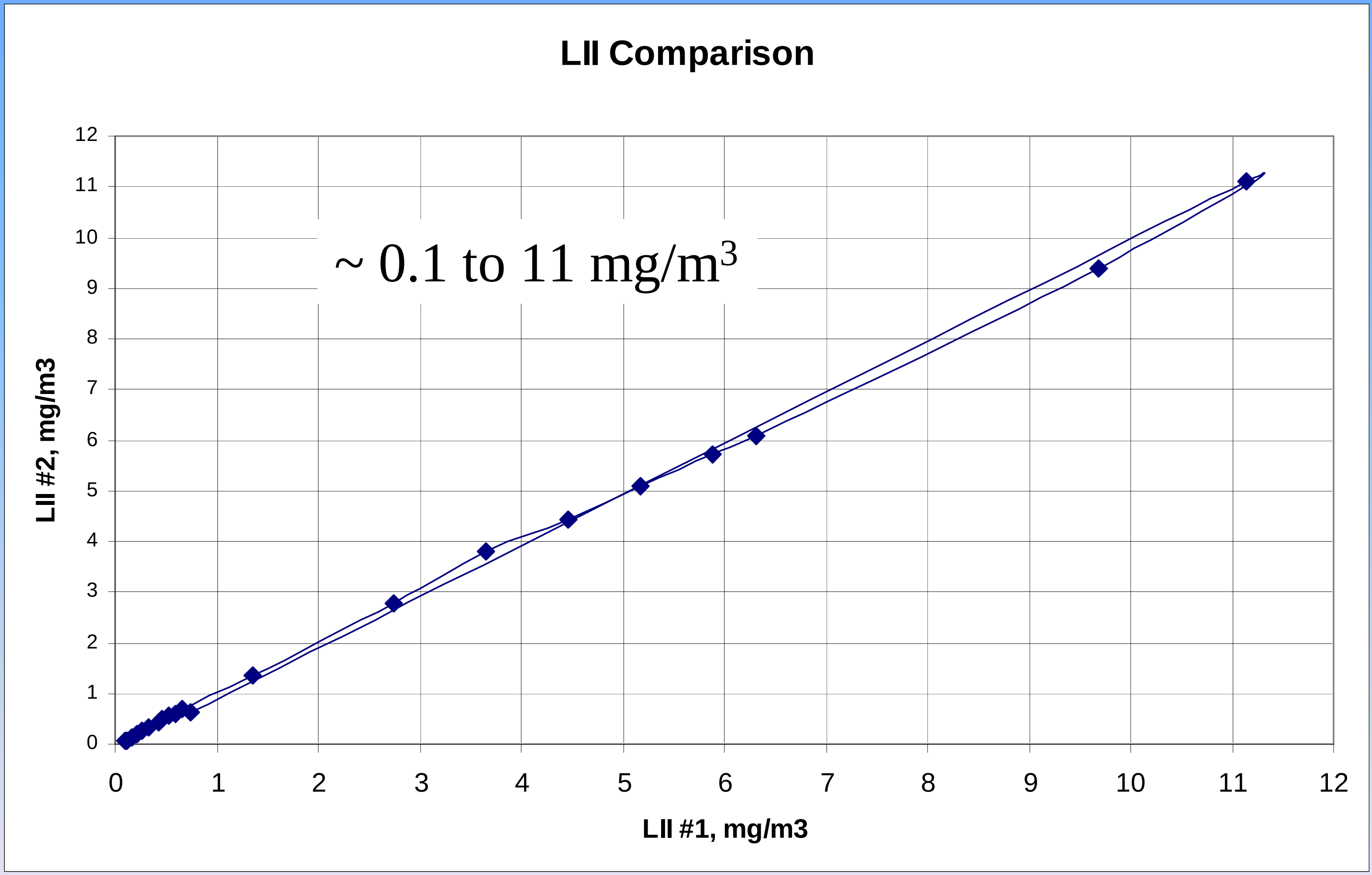
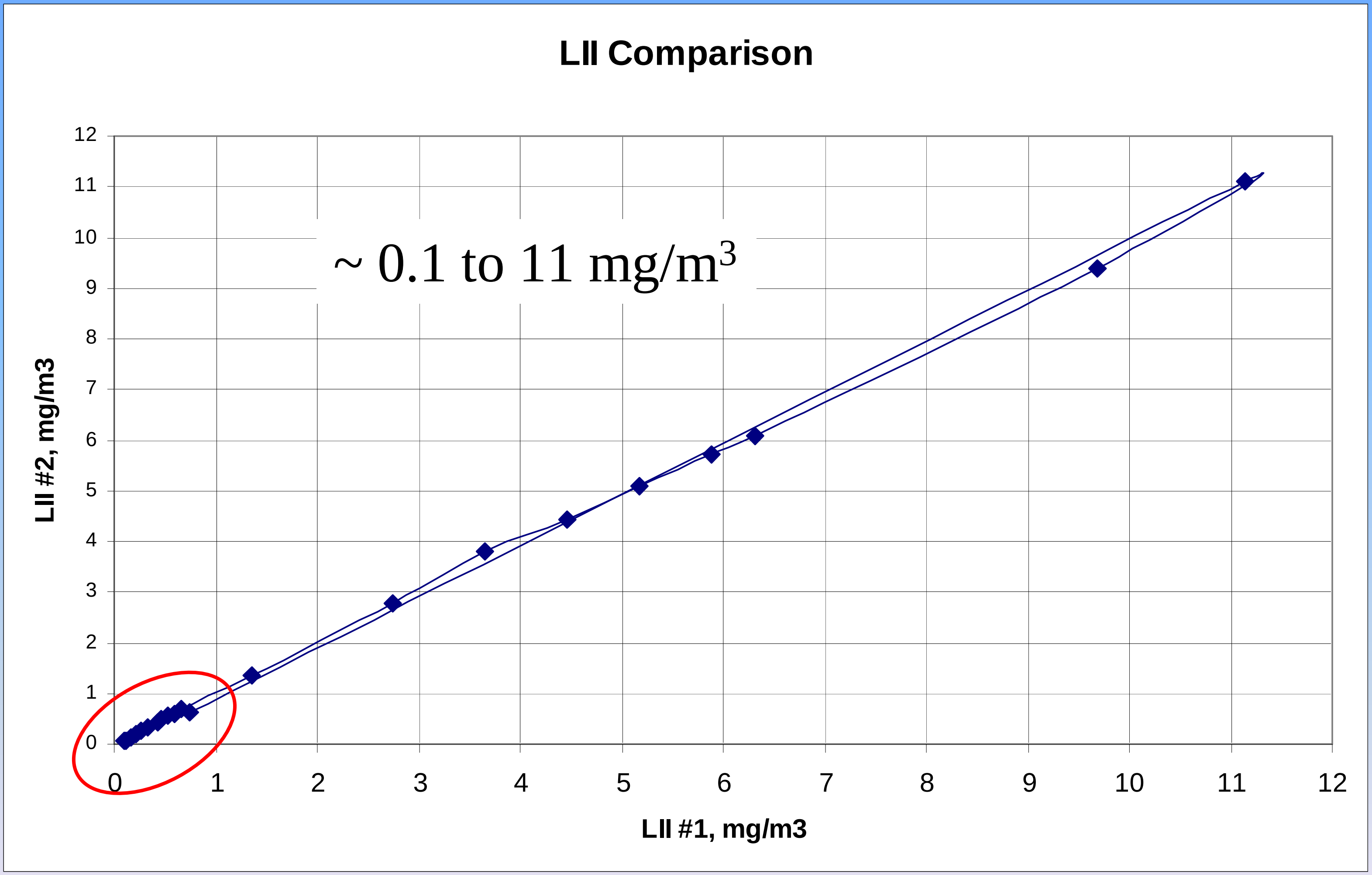
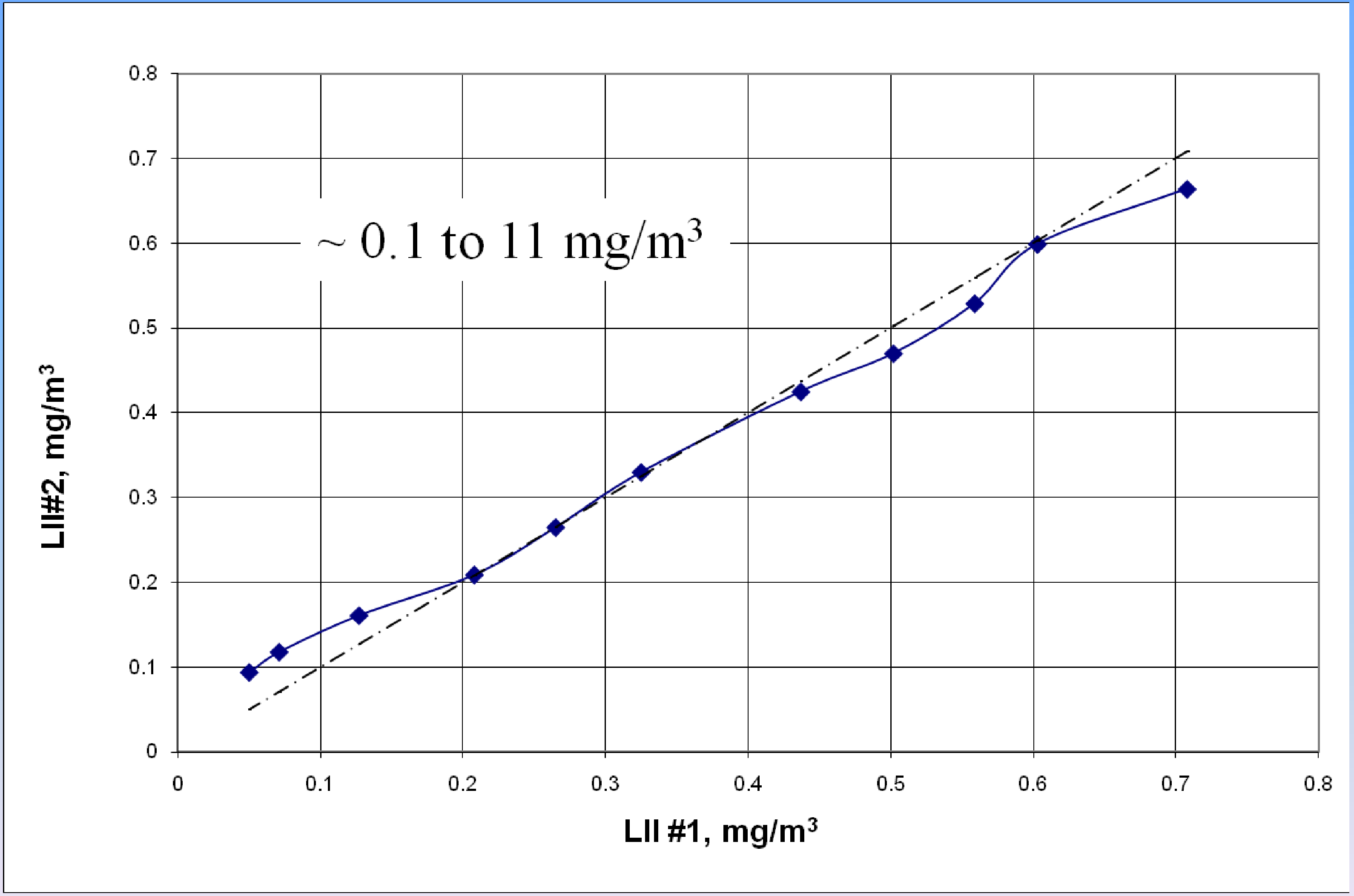
LII-200 Instrument Comparison



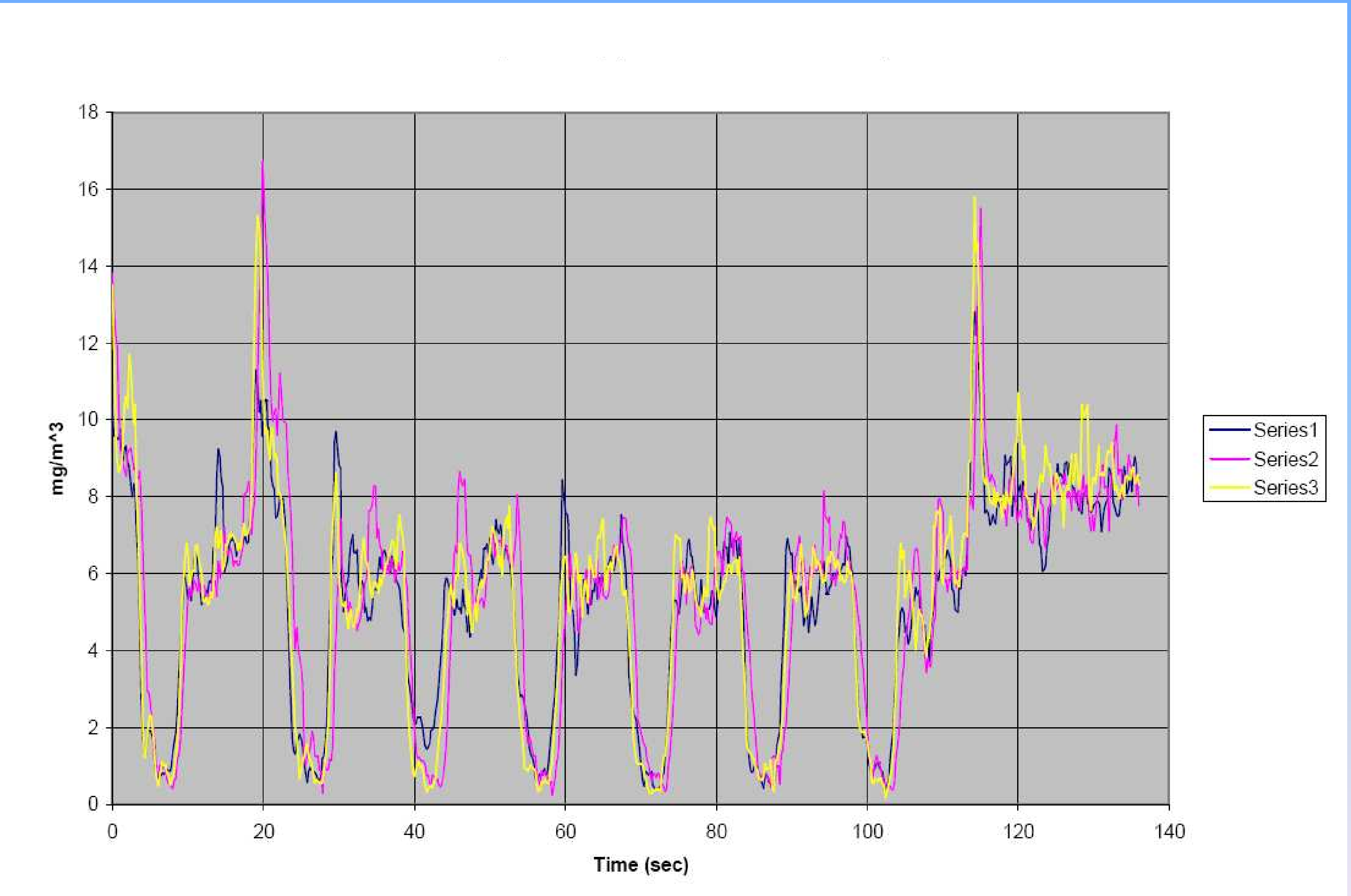
LII-200 Instrument Comparison



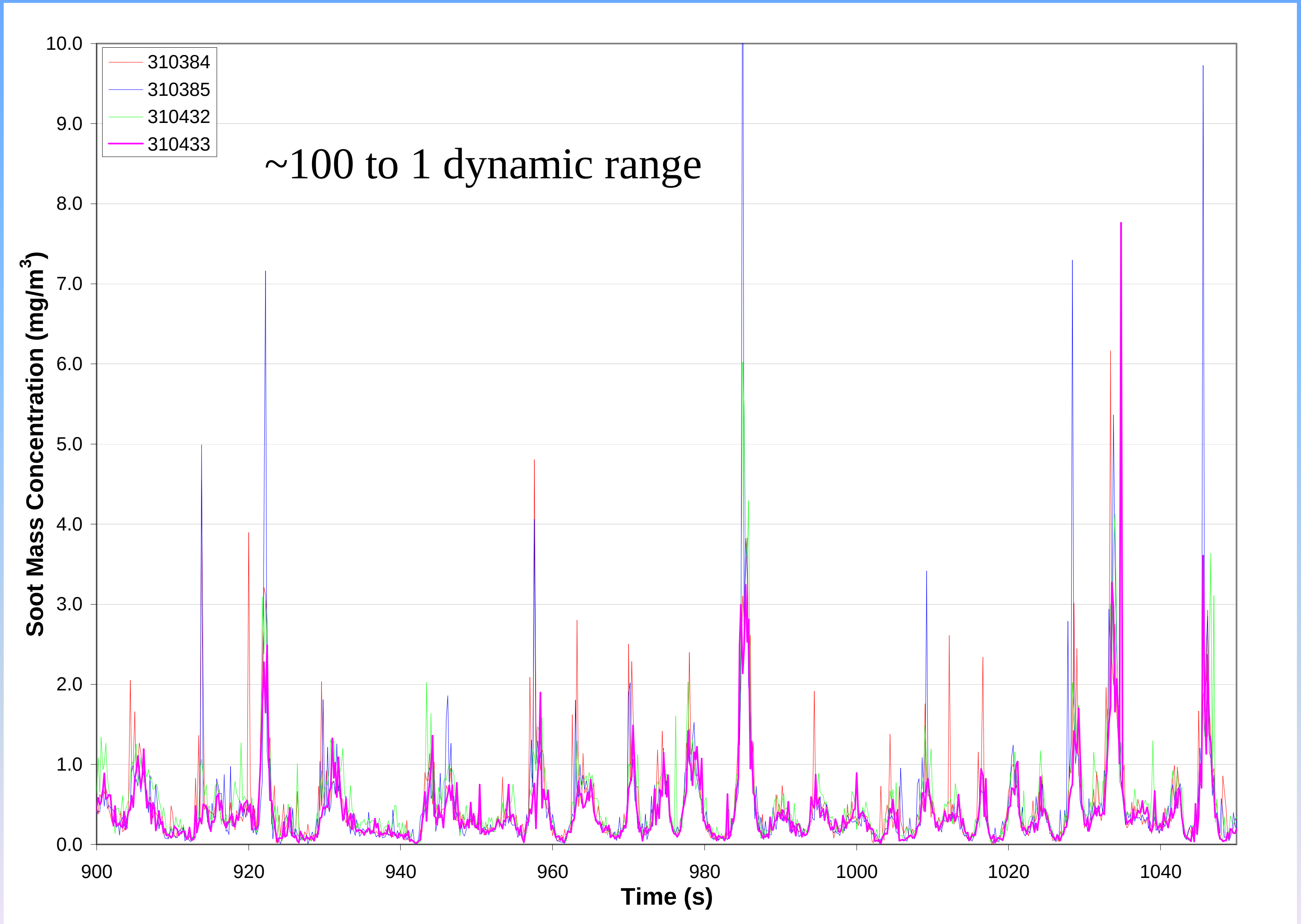
LII-200 Instrument Comparison



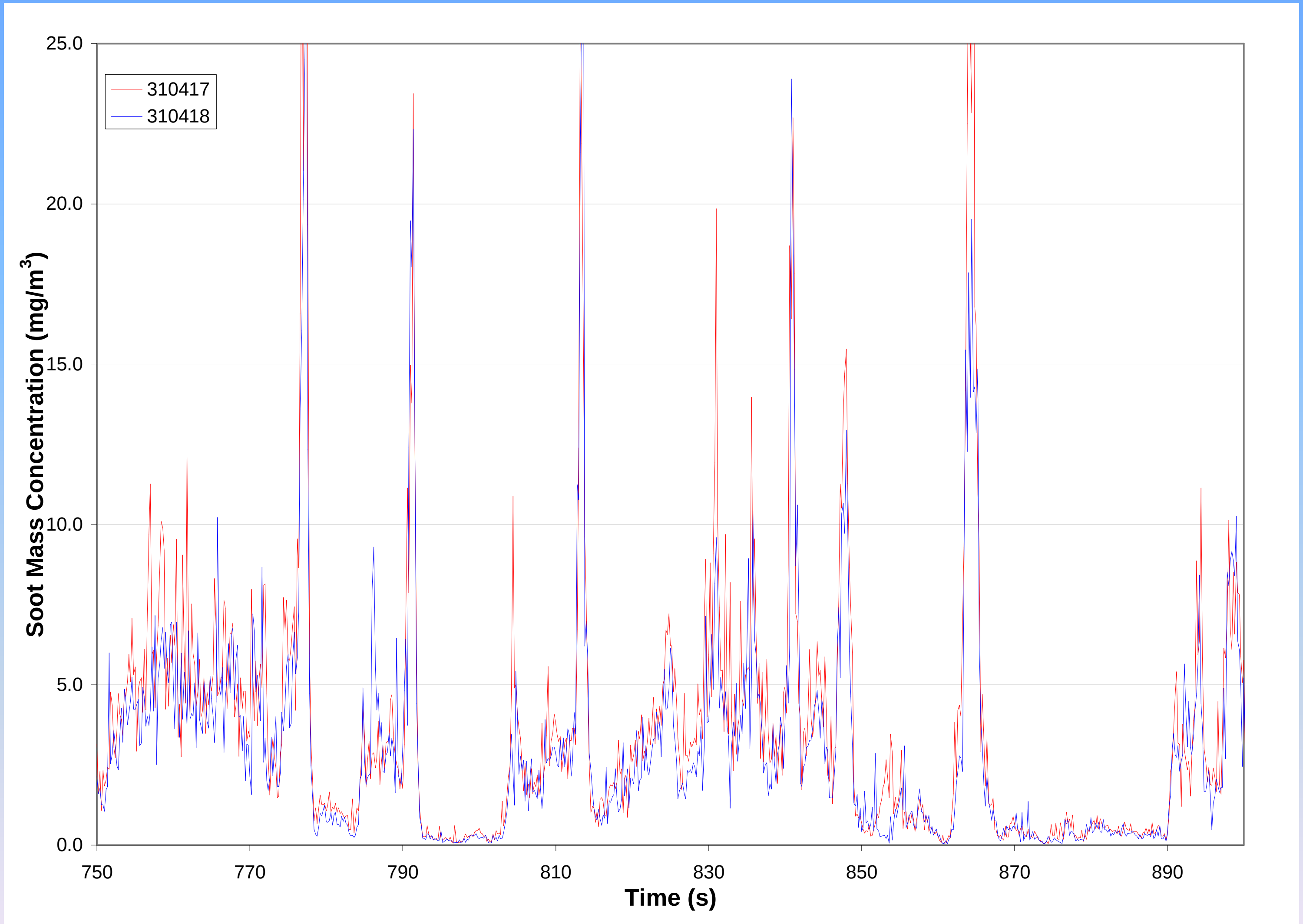
Diesel Cycle Measurement Repeatability



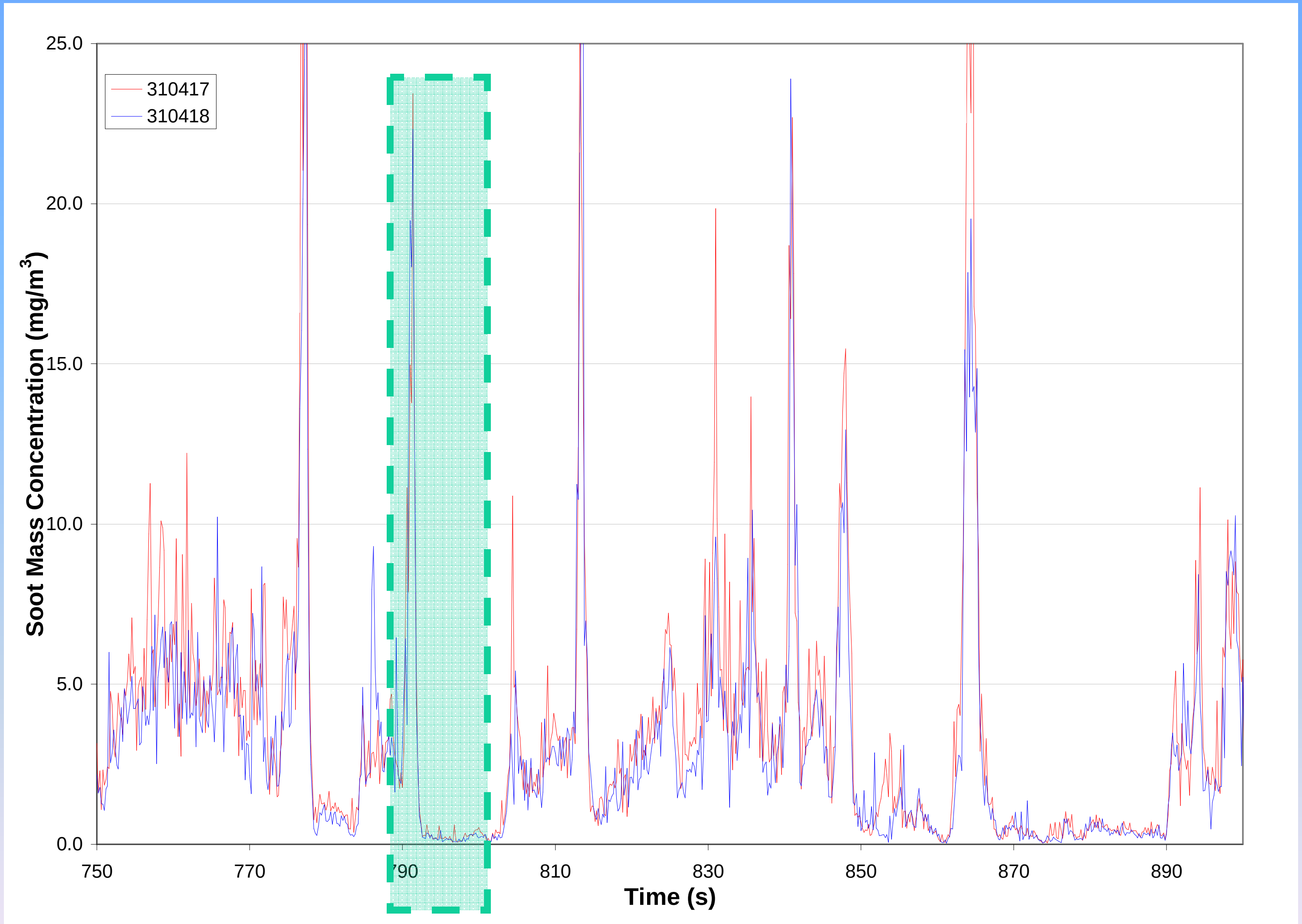
Section of Diesel FTP Cycle from Dilution Tunnel, 4 Repeats



Raw Exhaust (600-750s – 2 repeats)



Raw Exhaust (600-750s – 2 repeats)



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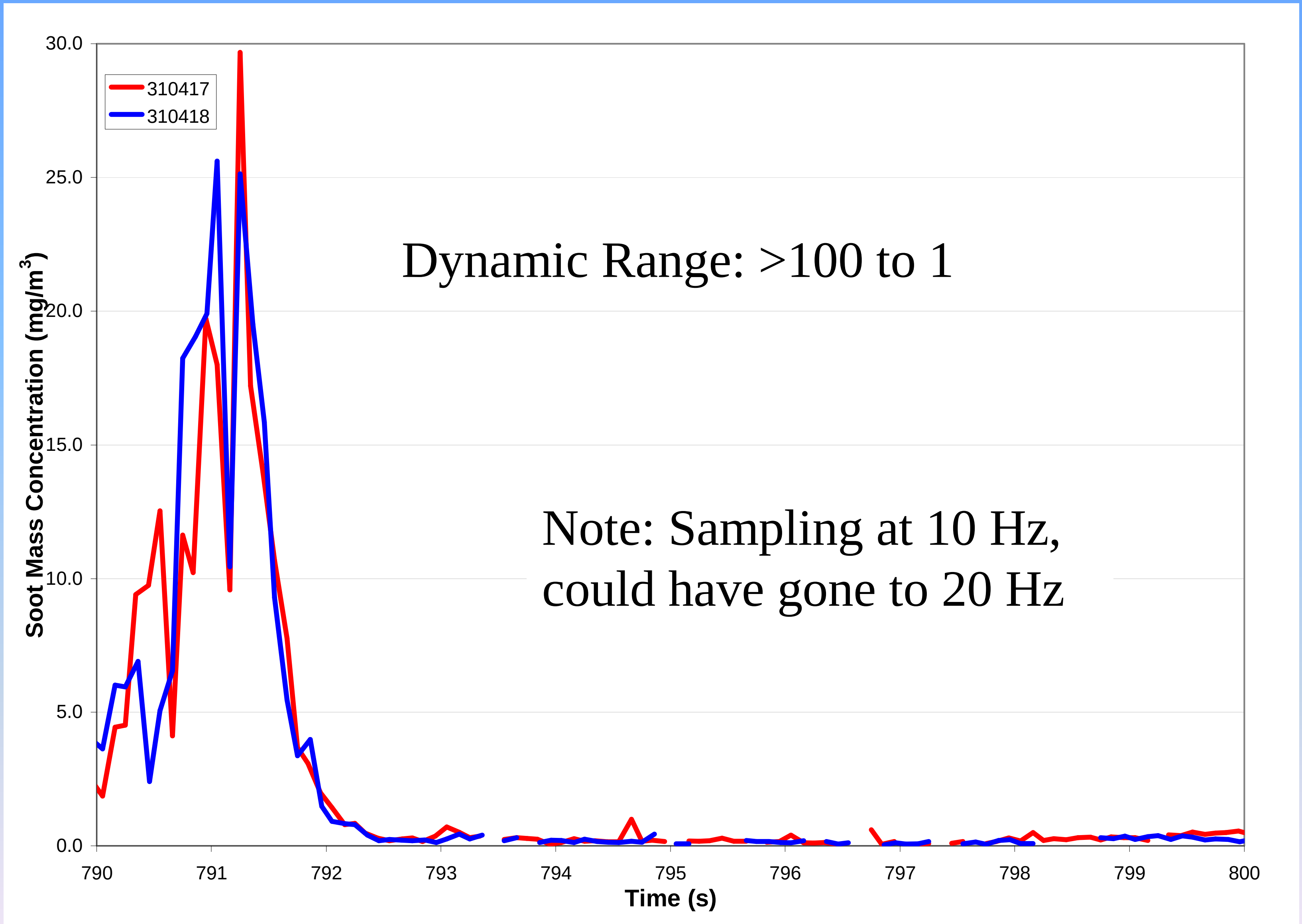
Raw Exhaust (790-800s – 2 repeats)



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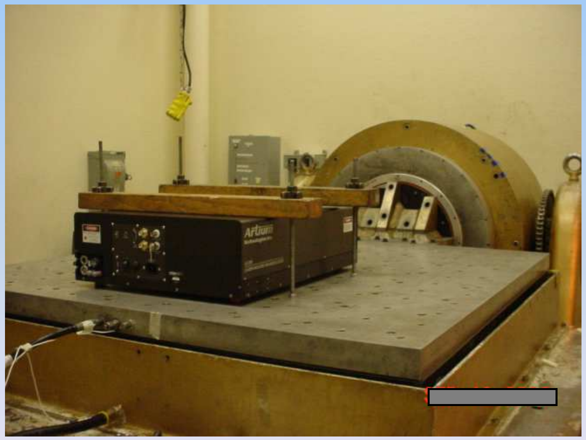
LII Optics Subjected to Mil Spec Vibration Testing

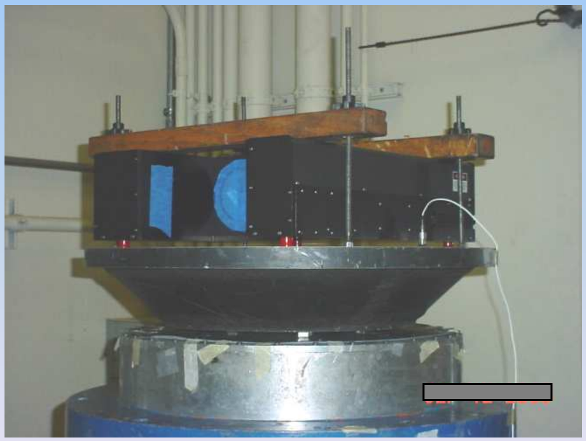
MIL-STD-810F Method 516.5 – Shock

Preparation for On road and Helicopter Flight Tests



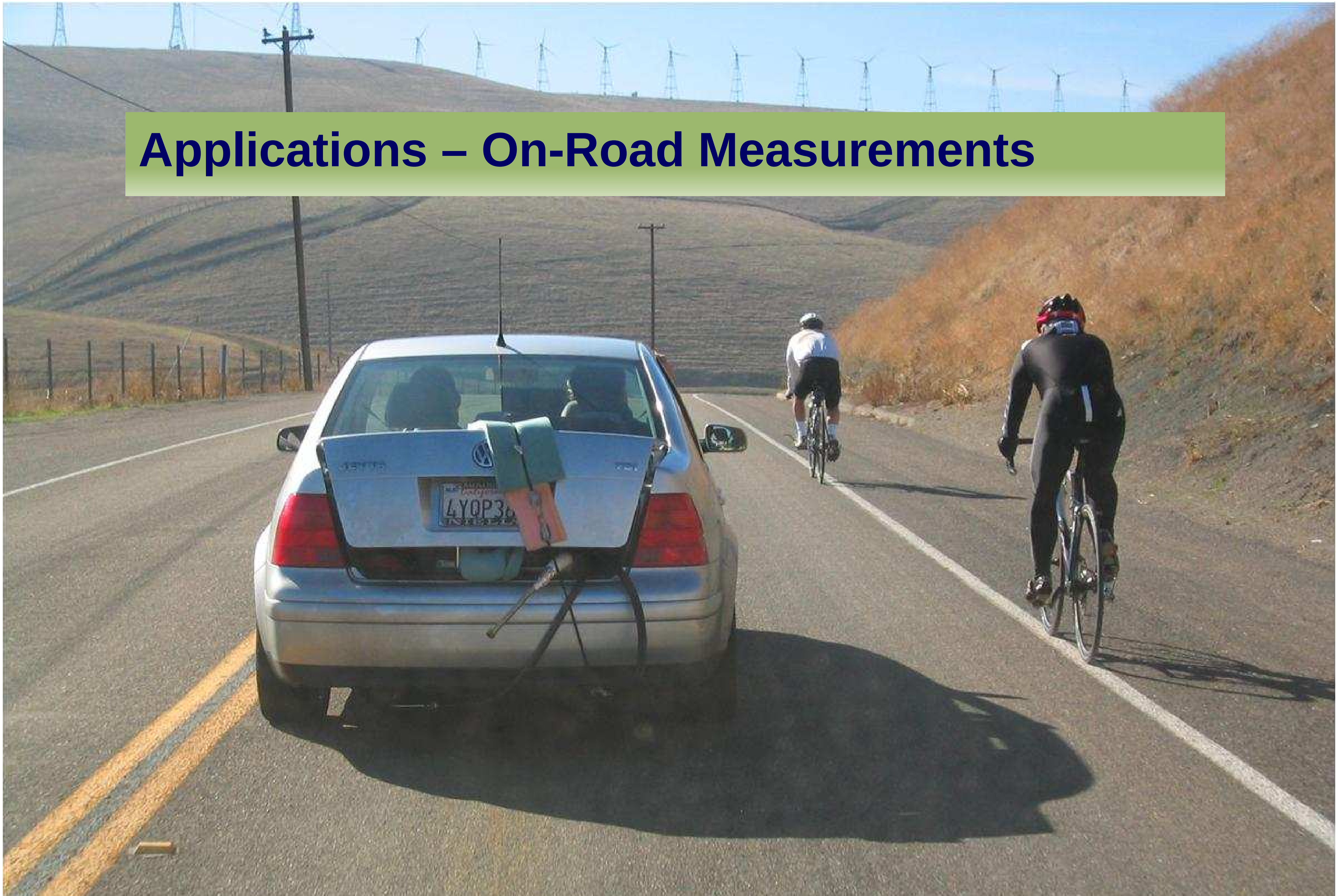
X Axis

Y Axis



Z Axis

Applications – On-Road Measurements



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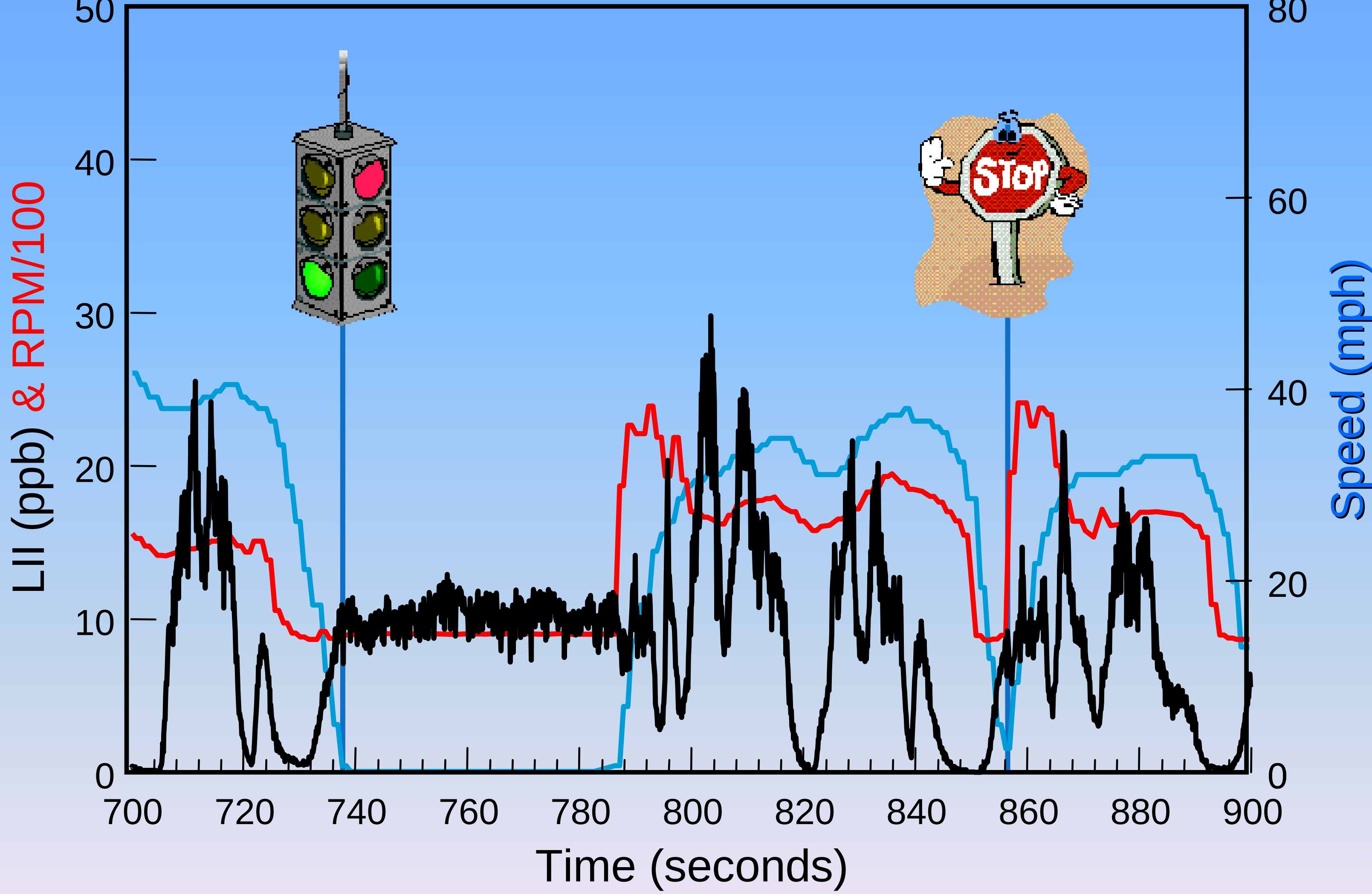
Spray Diagnostics

Particulate Emissions

Cloud Research

VW TDI: Stop-Start Urban Driving



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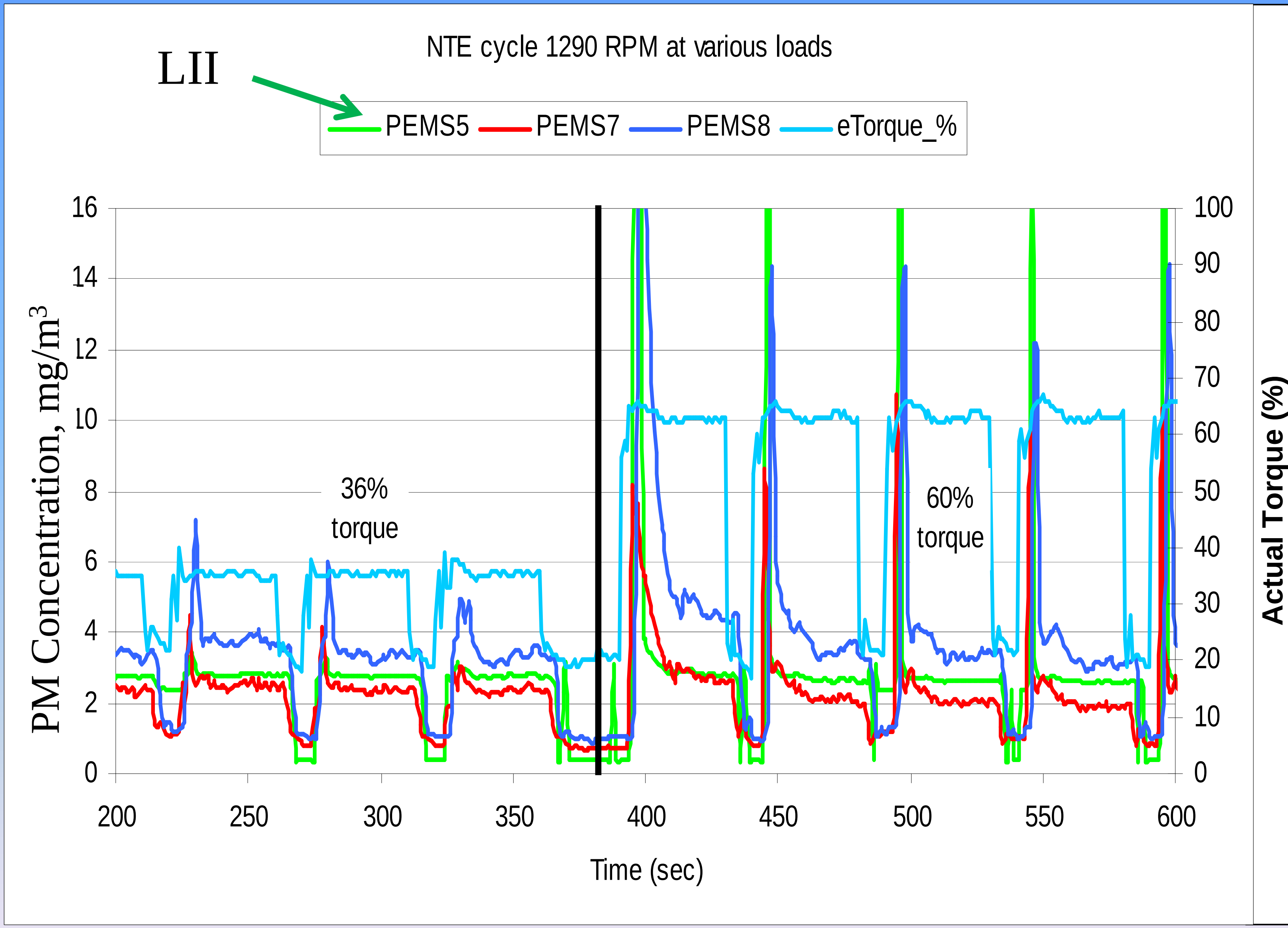
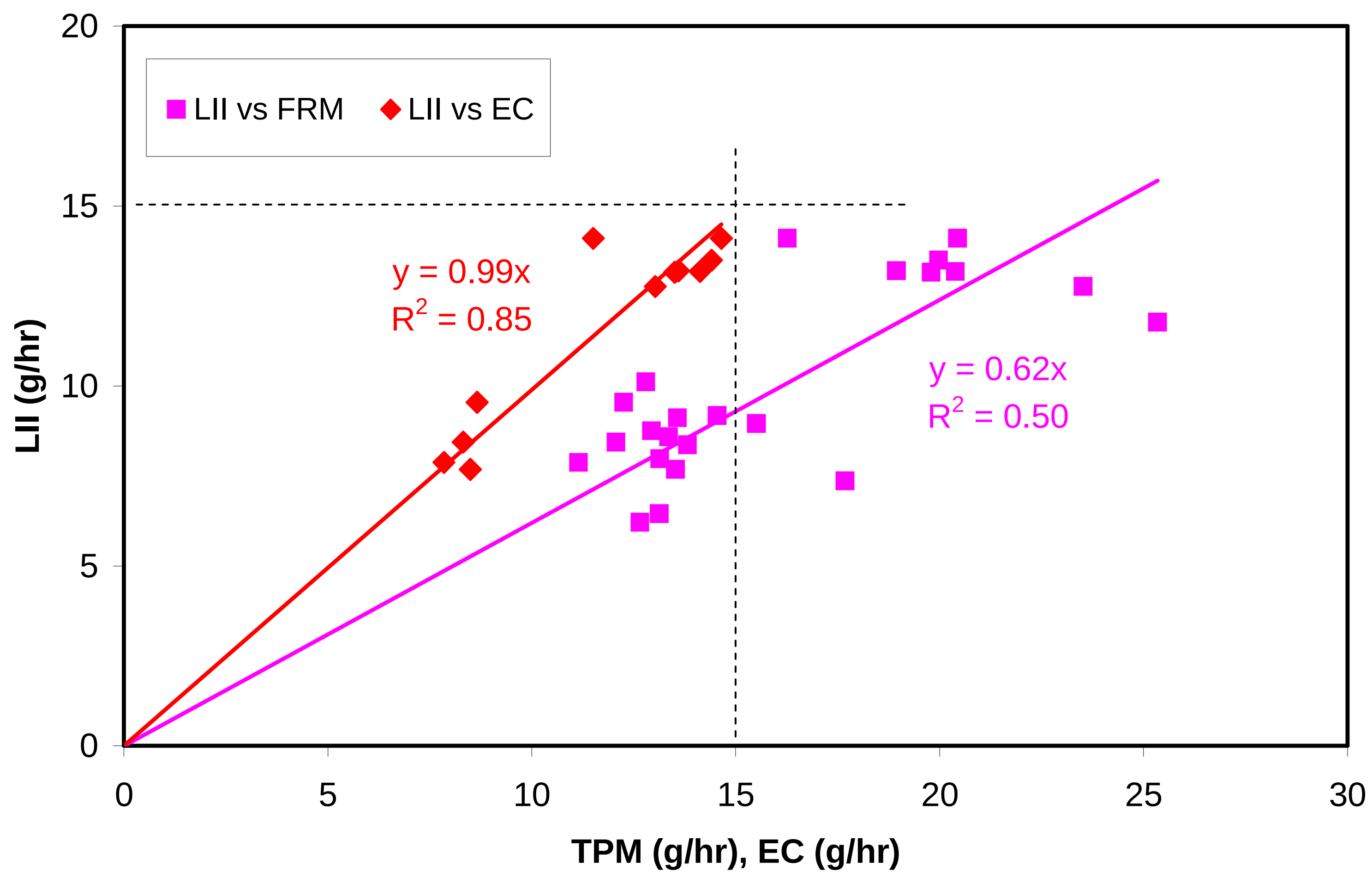


Test time (seconds)

CARB: Heavy-Duty Diesel NTE Summary



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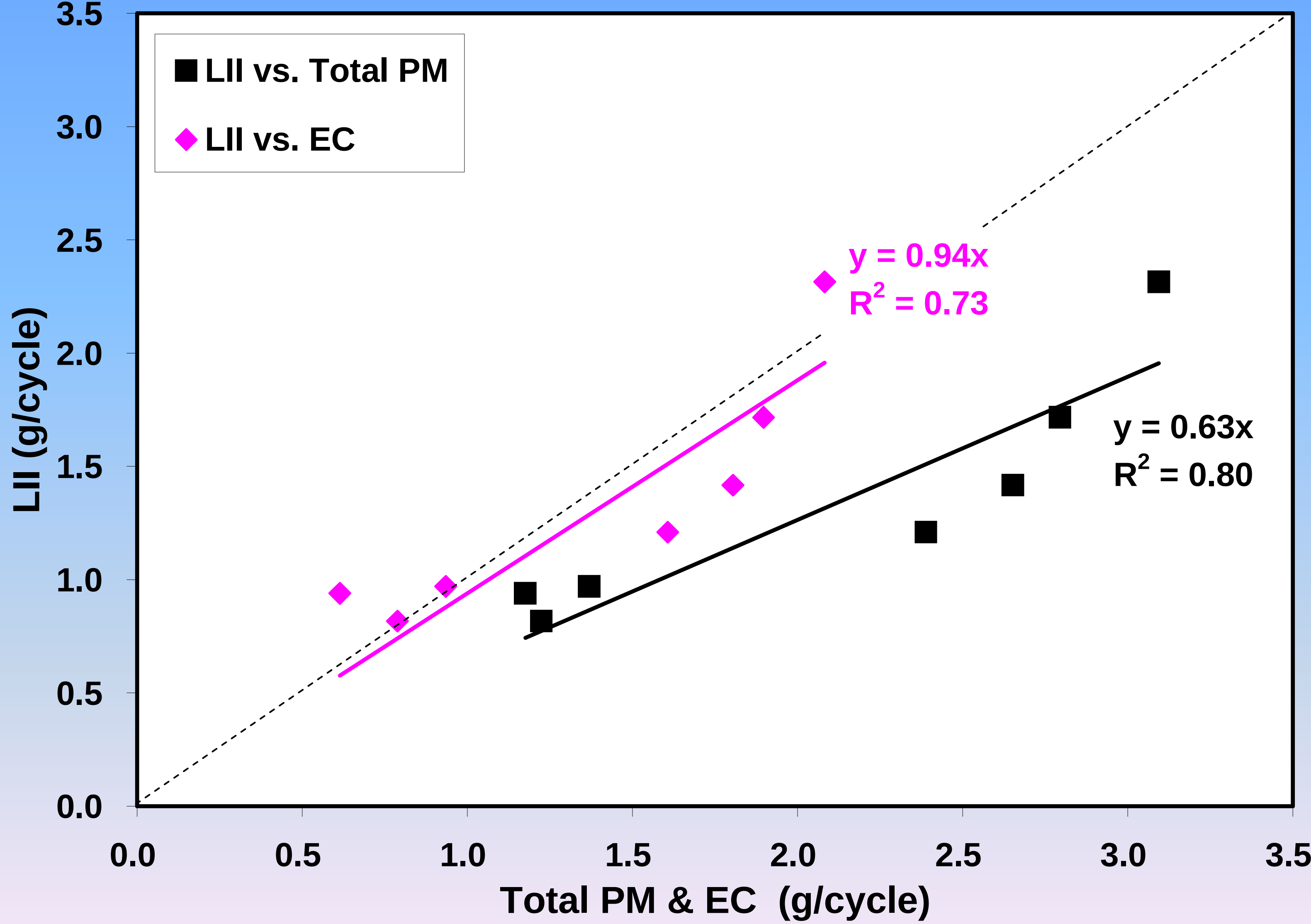
CARB: Heavy-Duty Diesel On-Road Summary



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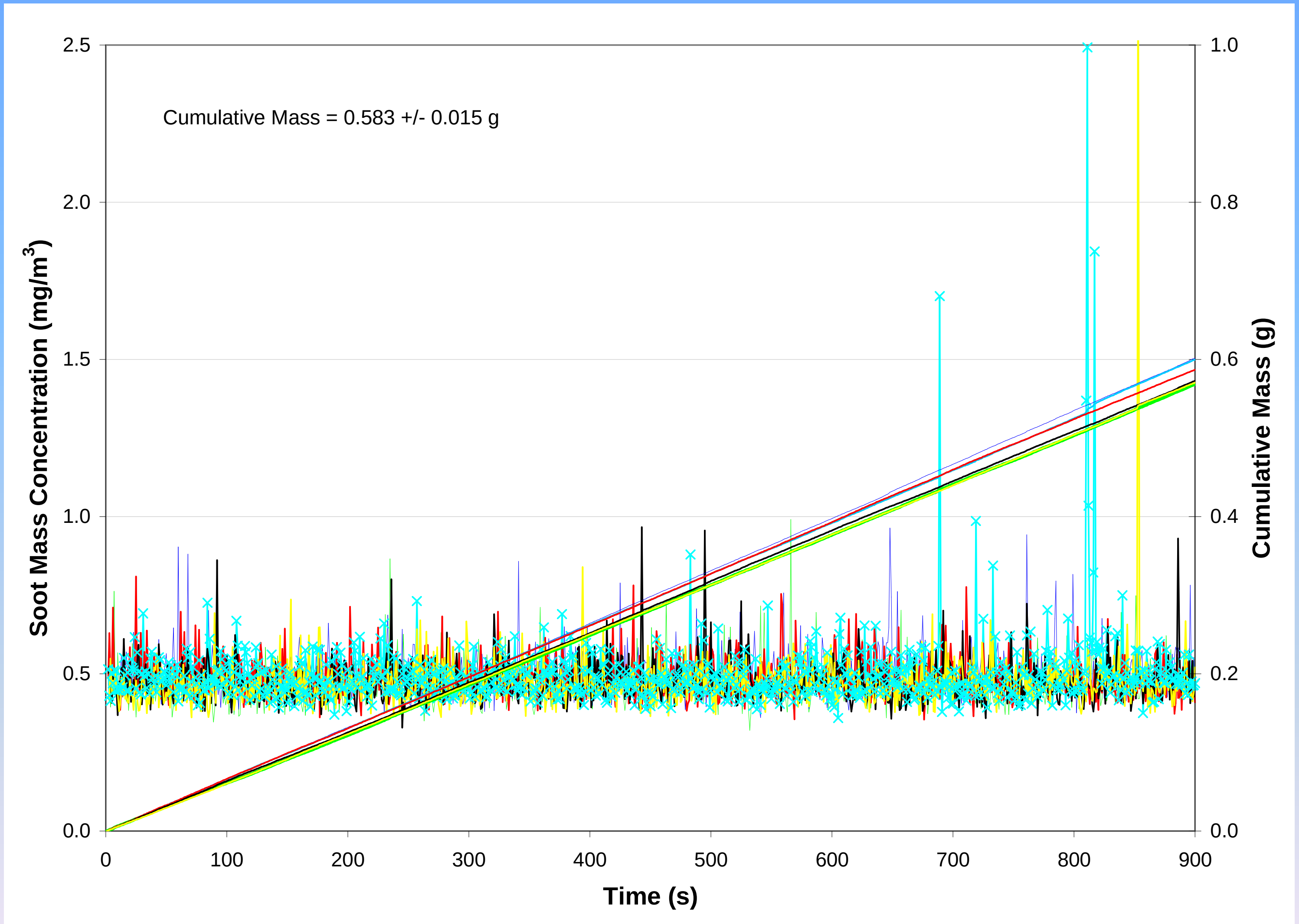
HDDM2 – Steady State – 6 Repeats



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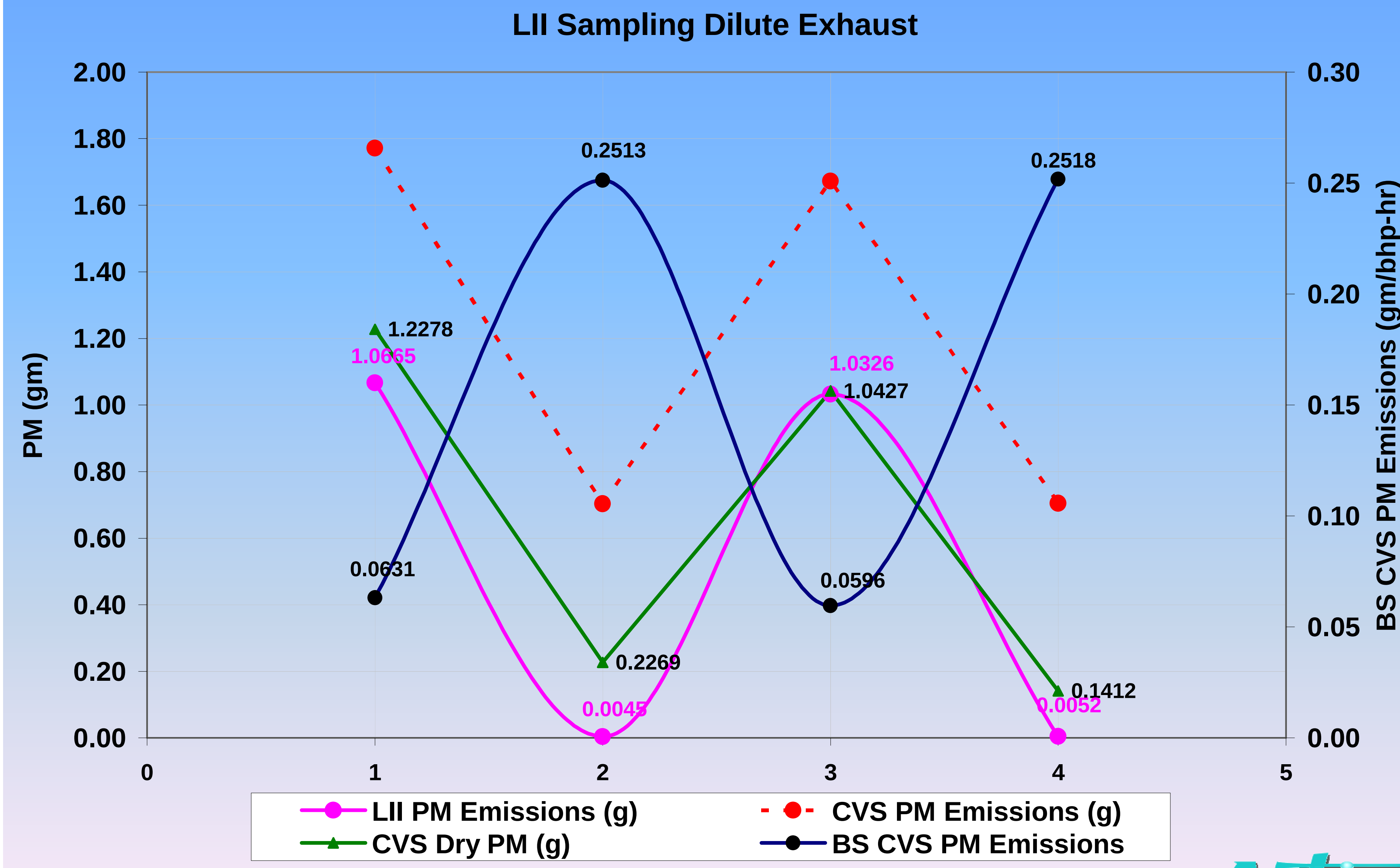
HDDM1 – Dilute Exhaust



testing at Cummins

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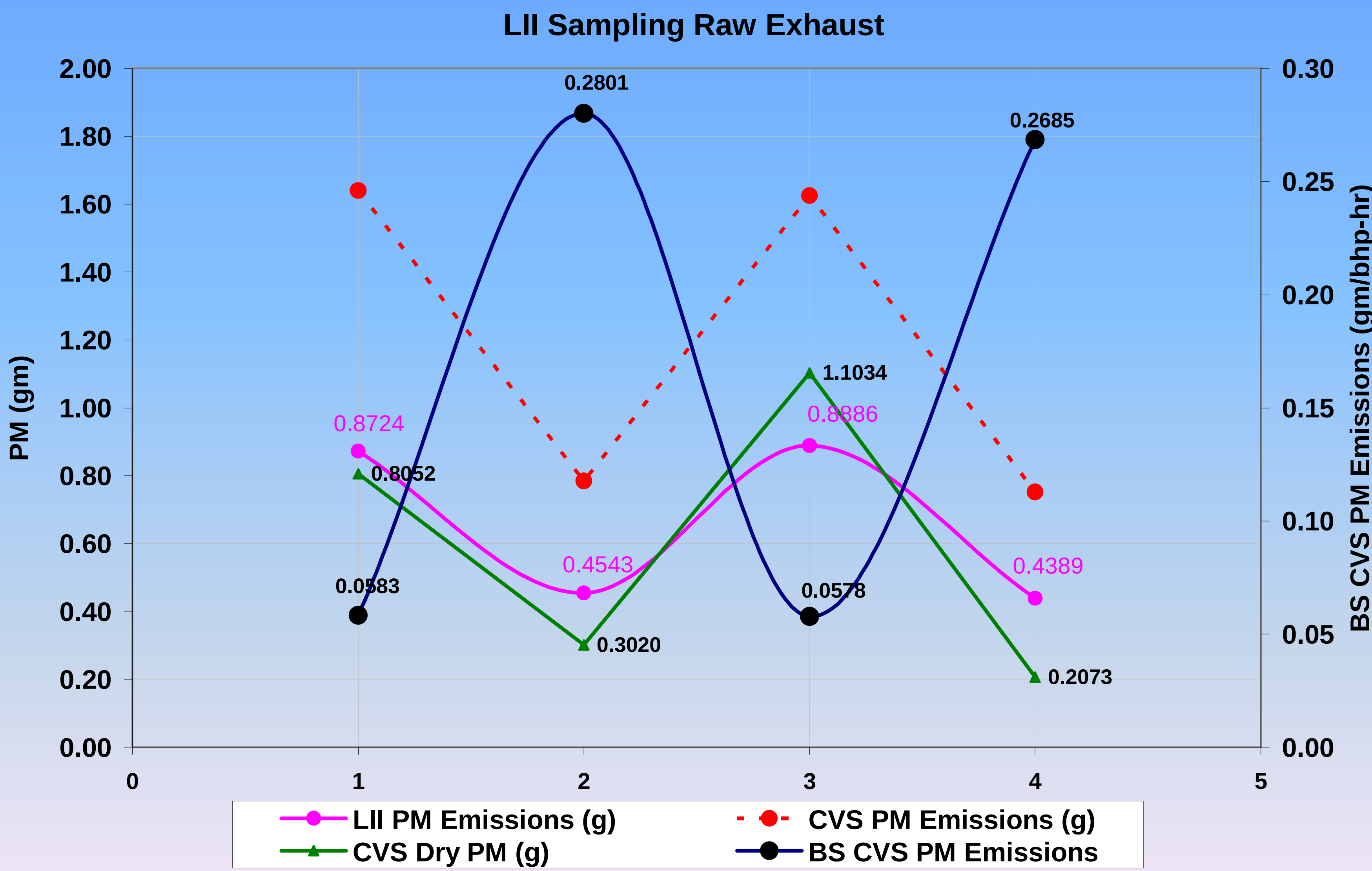
HDDM1 – Raw Exhaust



testing at Cummins

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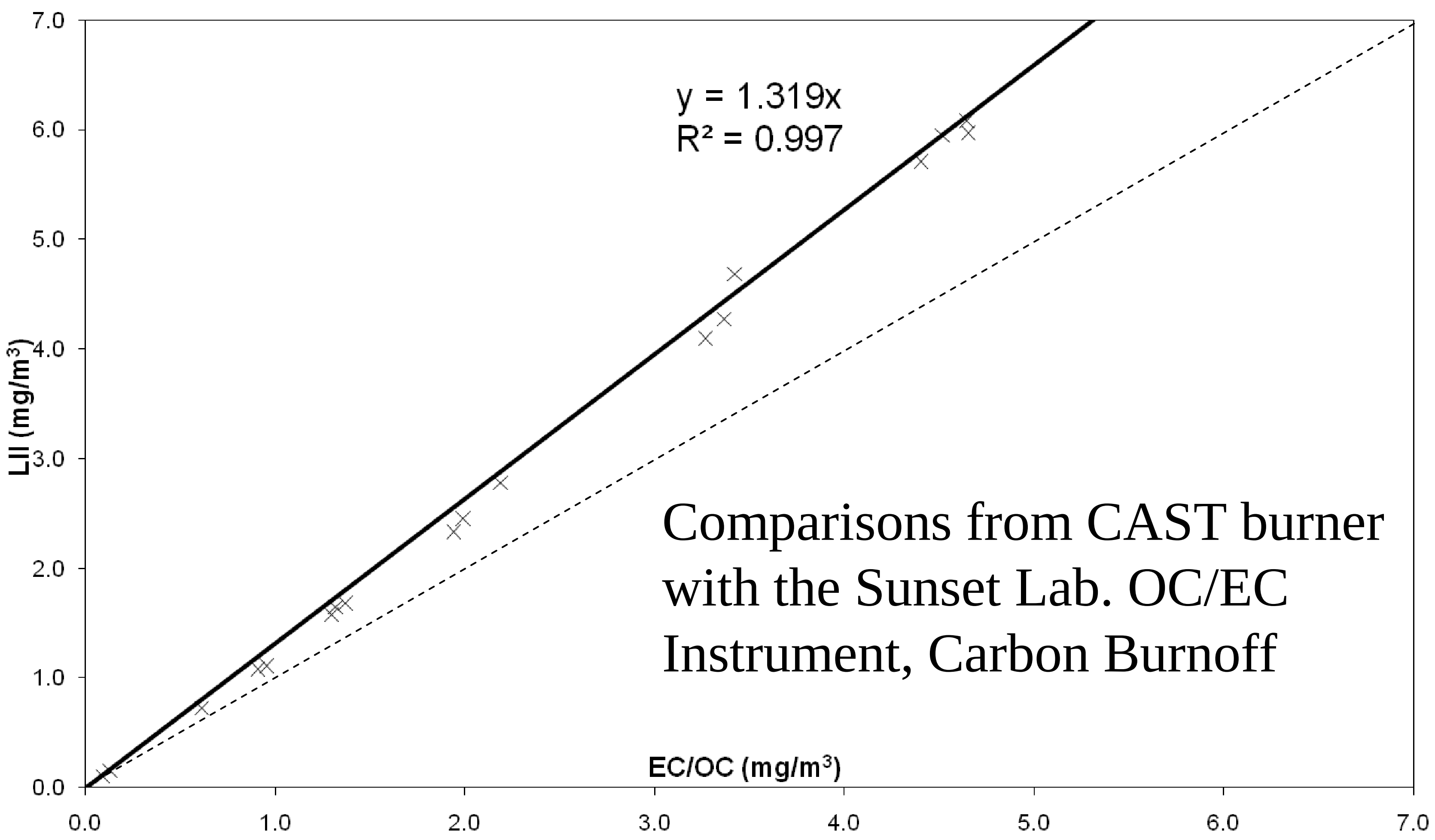
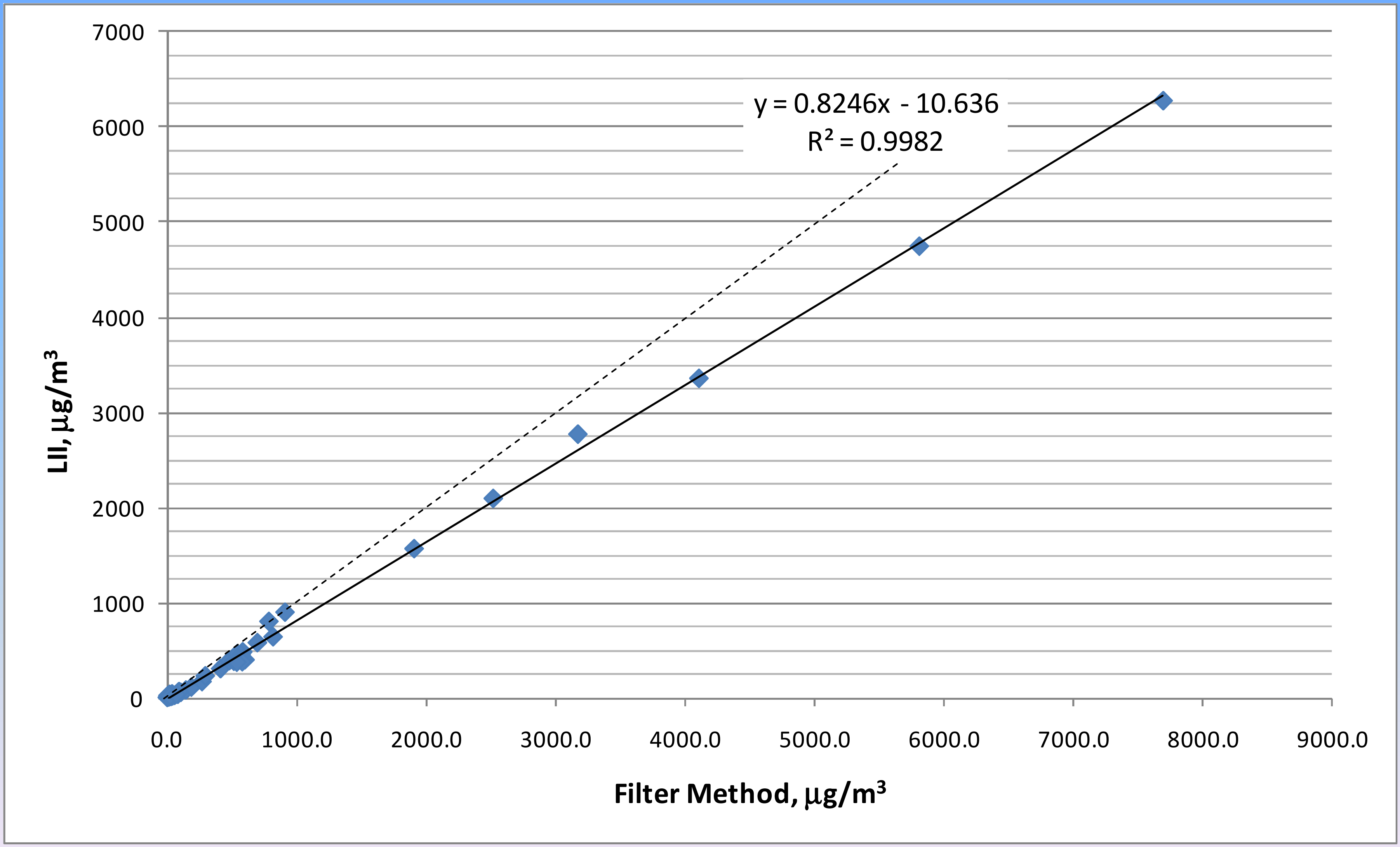
SwRI Instrument Comparisons



Comparisons from CAST burner with the Sunset Lab. OC/EC Instrument, Carbon Burnoff

NASA Glenn Research Center tests conducted on soot from a mini-CAST burner in December 2009 prior to measuring gas turbine particulate emissions



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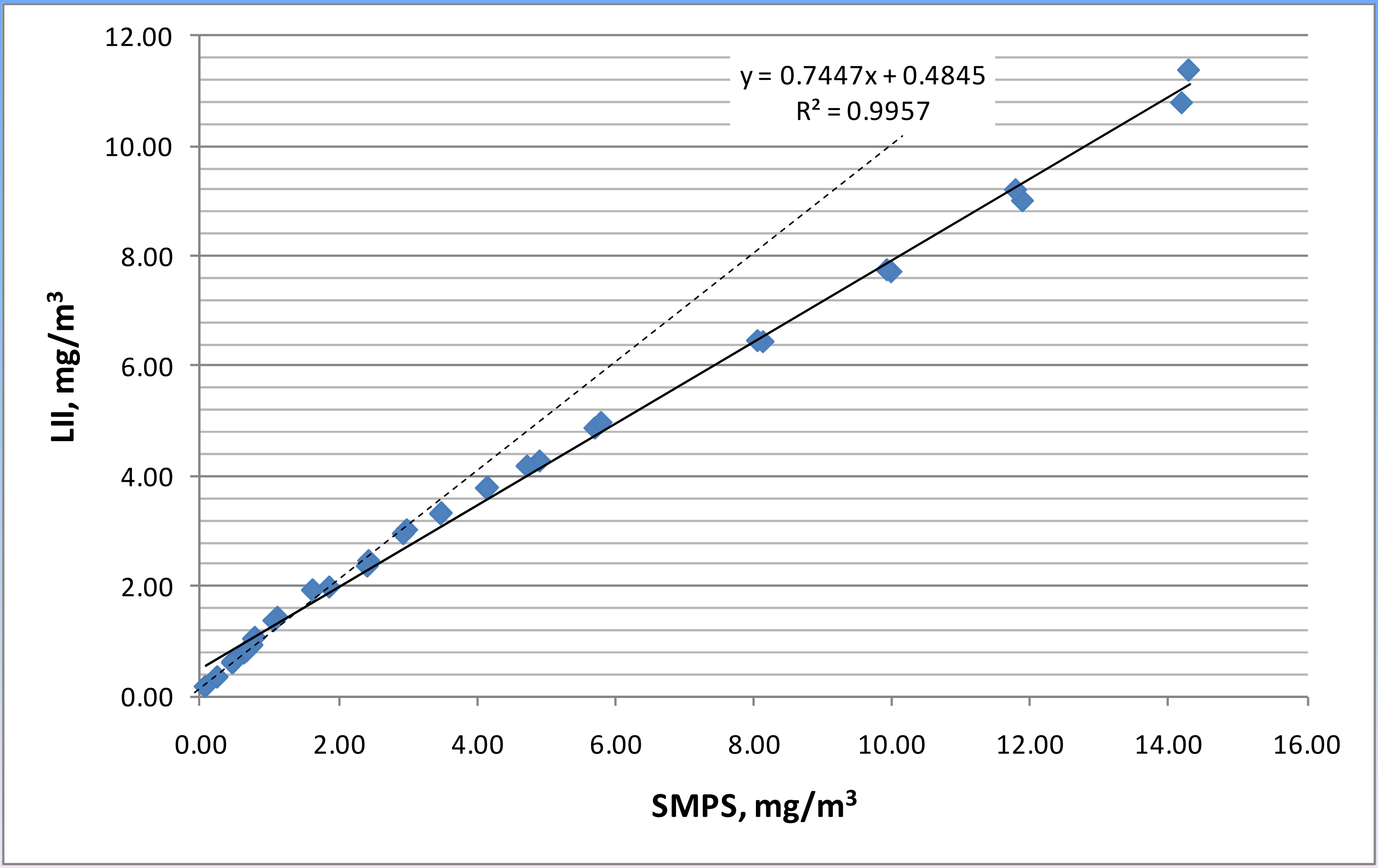
NASA Glenn measurements of soot generated by the mini-CAST burner and compared to the TSI SMPS measurements.

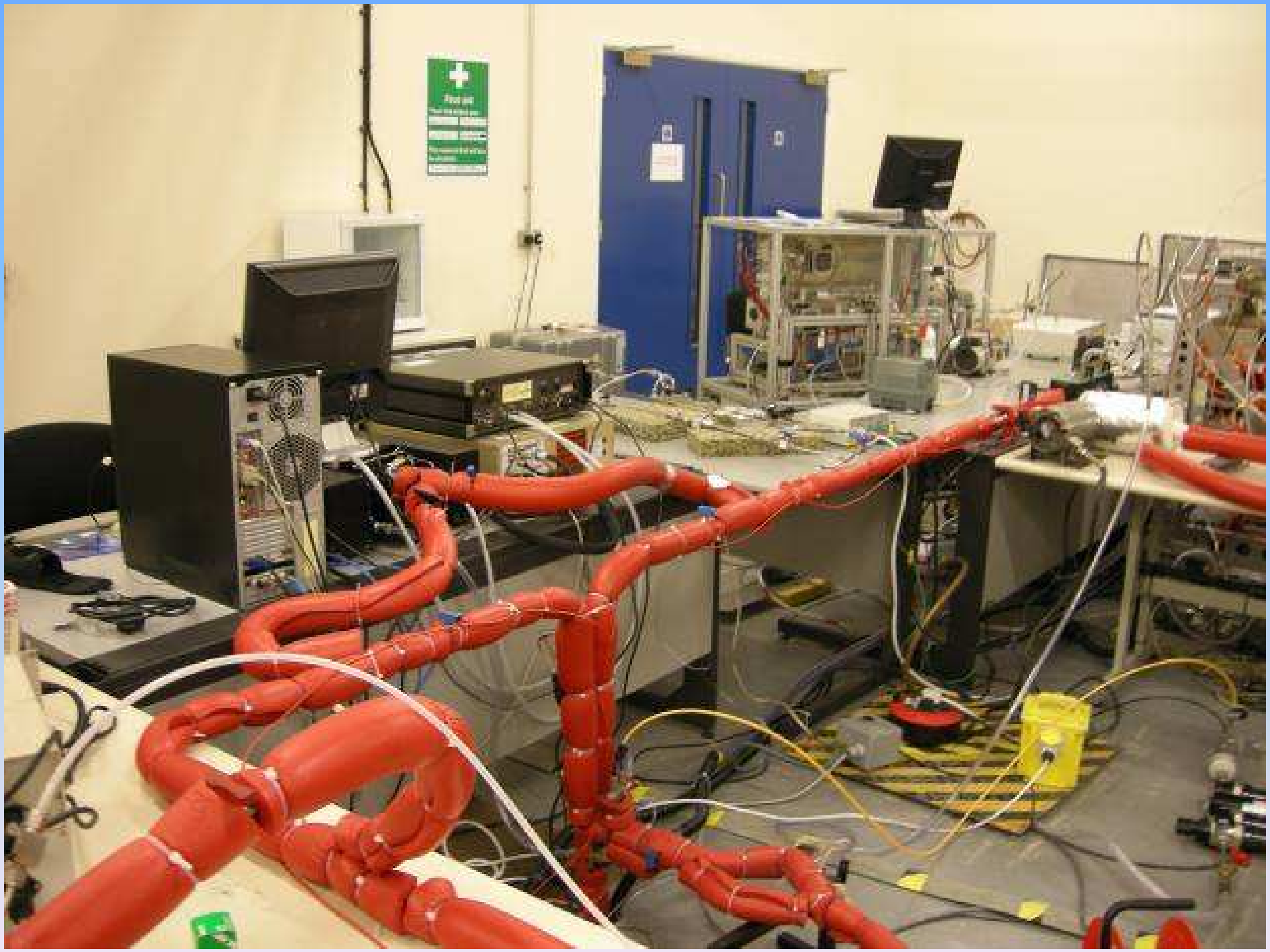


The Mystery of Inconsistent LII Measurements

Observations:

- During some tests, LII showed variances from run to run
- Poor agreement with gravimetric
- Poor agreement with MAAP and other filter-based instruments
- Large spikes in time svf history

Sampling and Measurement of Aircraft Particulate Emissions (SAMPLE)
Cardiff University, UK



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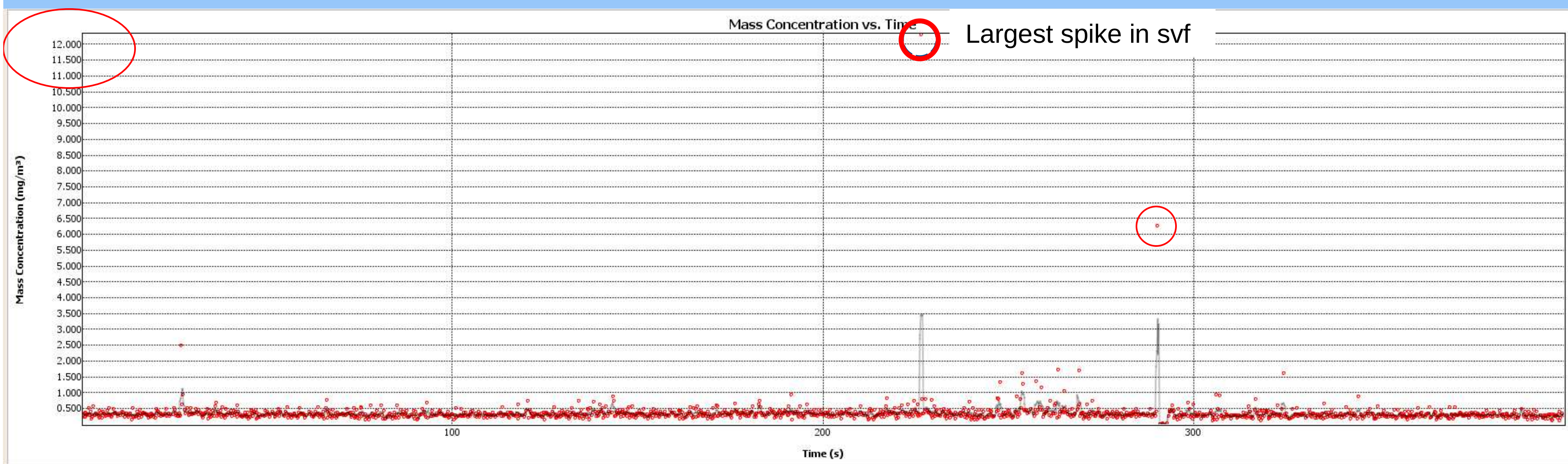
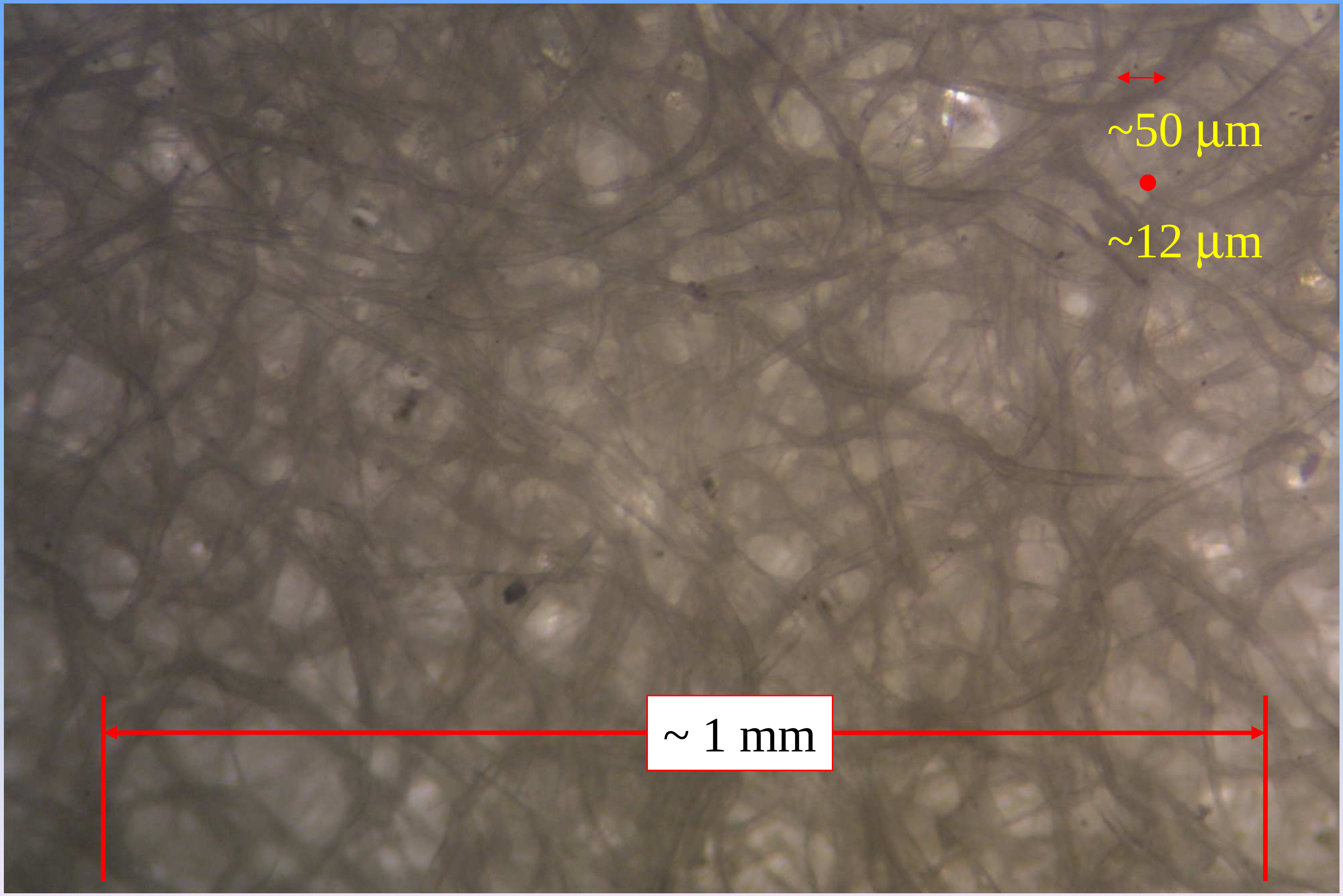
Observation: *SVF versus time plots show isolated spikes in the SVF values which cannot be accounted for as large concentrations of soot aggregates passing the sample volume. In the turbulent flow, such high concentration gradients do not exist for long.*

Each red dot represents an LII soot measurement



Photograph of the Filter under an Optical Microscope



Cardiff Tests 31-3-09 to 1-4-09

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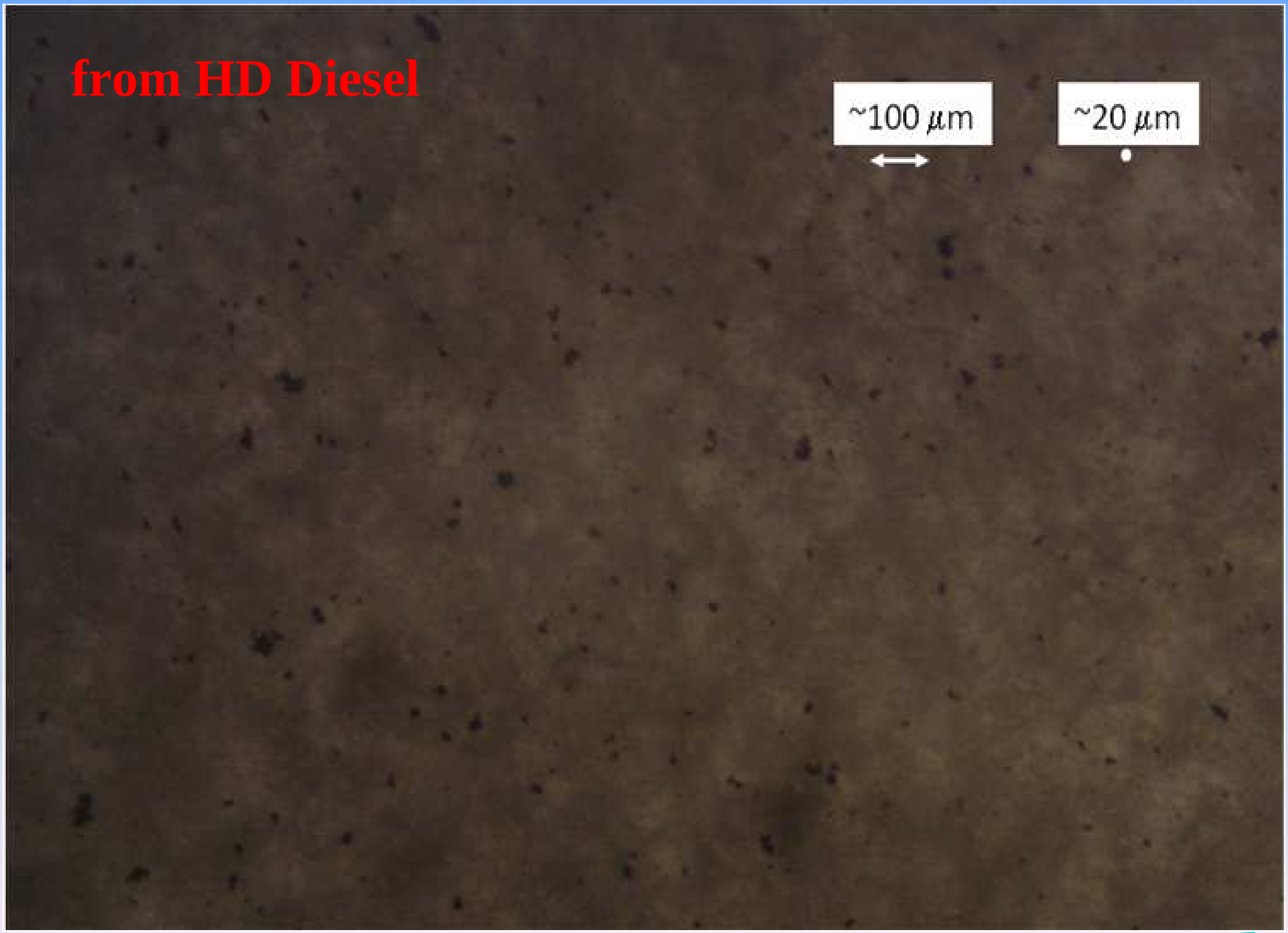
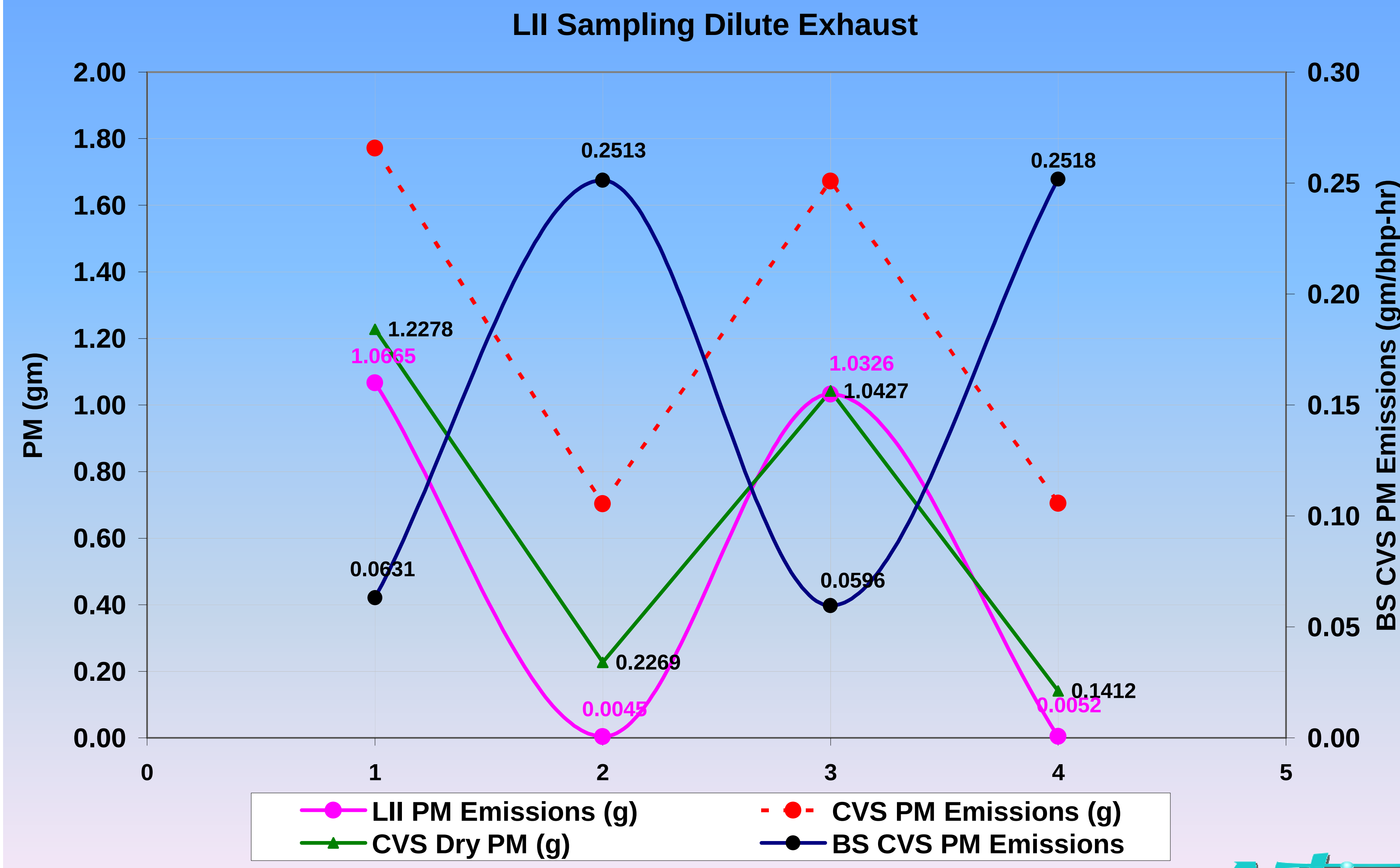
Sample contamination with large agglomerates of soot shed from sampling line surfaces



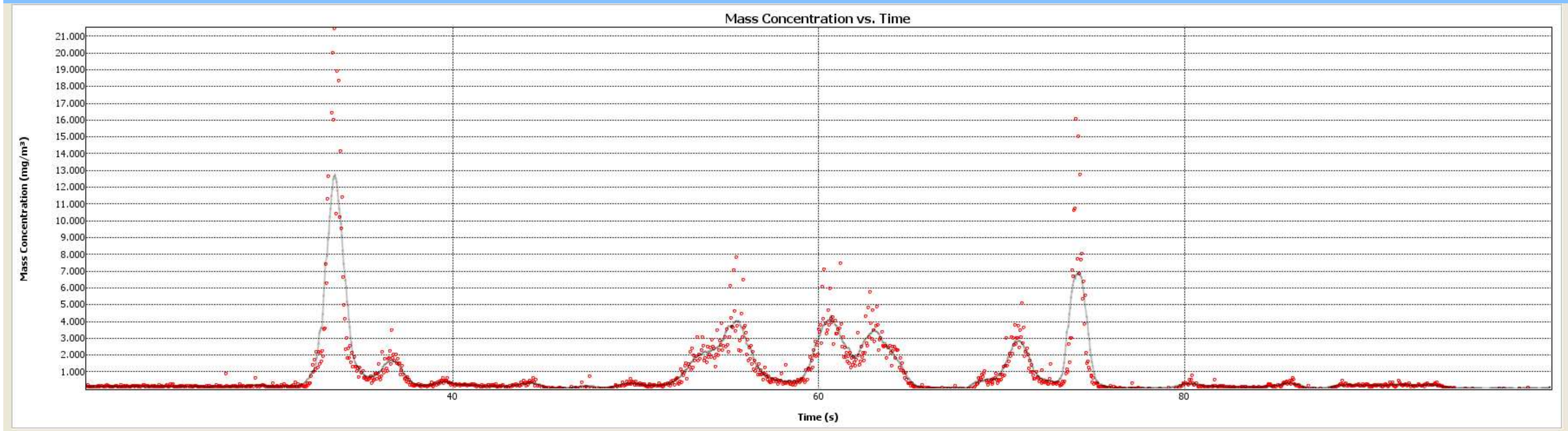
LII was Low in these tests, probably due to large agglomerates of soot



testing at Cummins

The Problem of Large Agglomerates

After cleaning the cyclone separator, a close observation of a section of the FTP cycle shows that the LII measurements consistently rise and fall shot to shot indicating that there are no individual spikes in the data. This implies that there are no large particles in the sample and so the results should agree with gravimetric.



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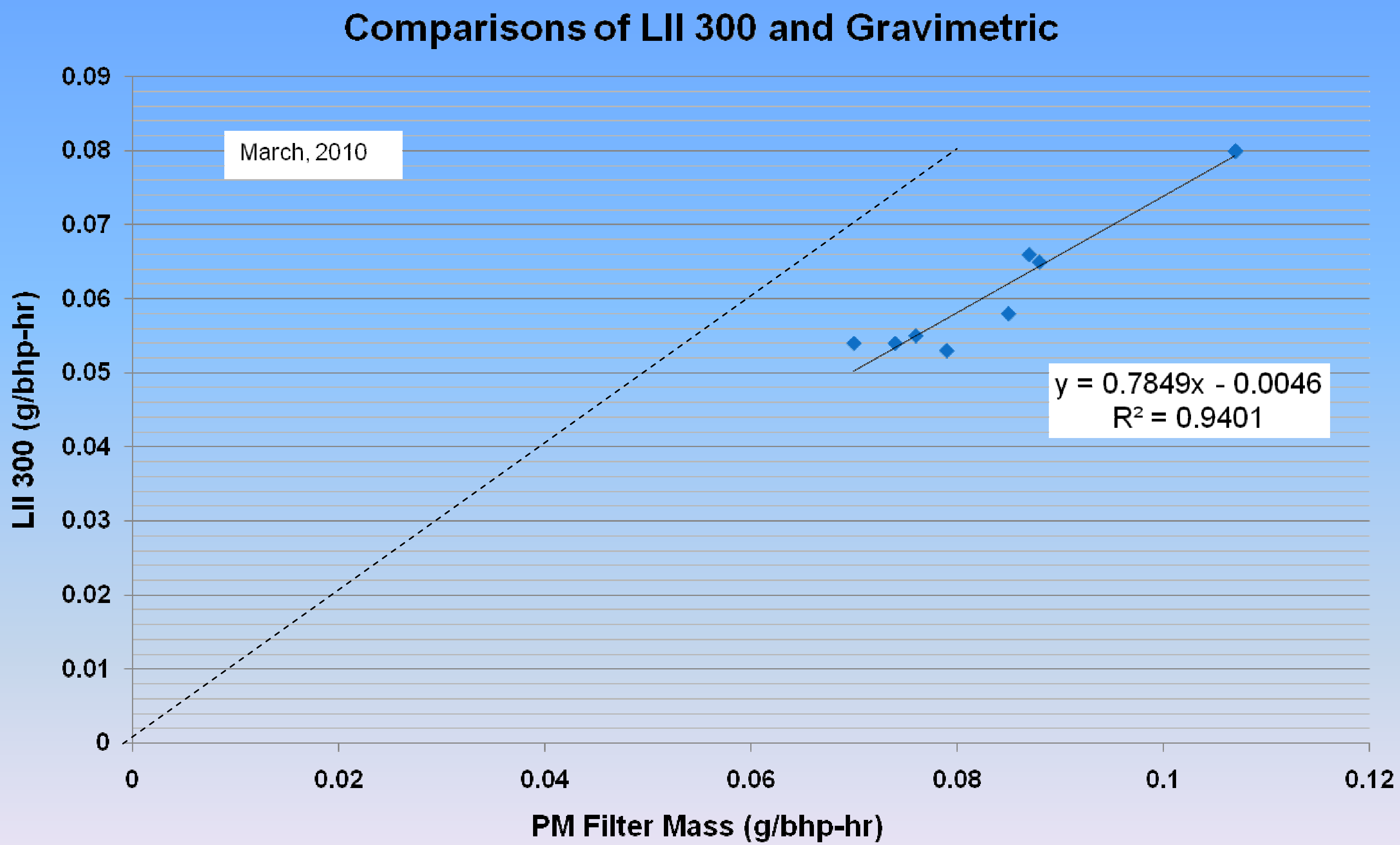
Recent Tests at Cummins



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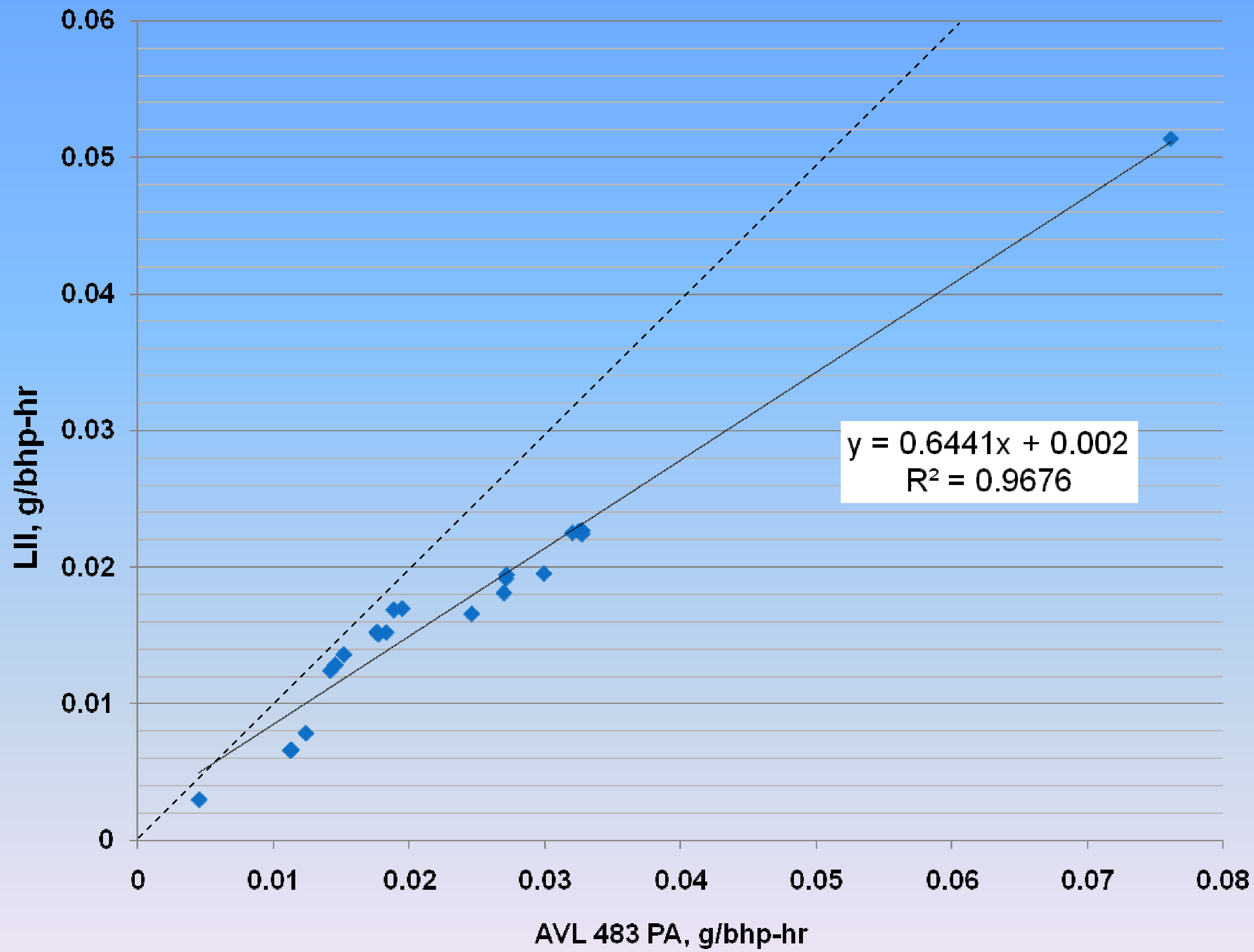
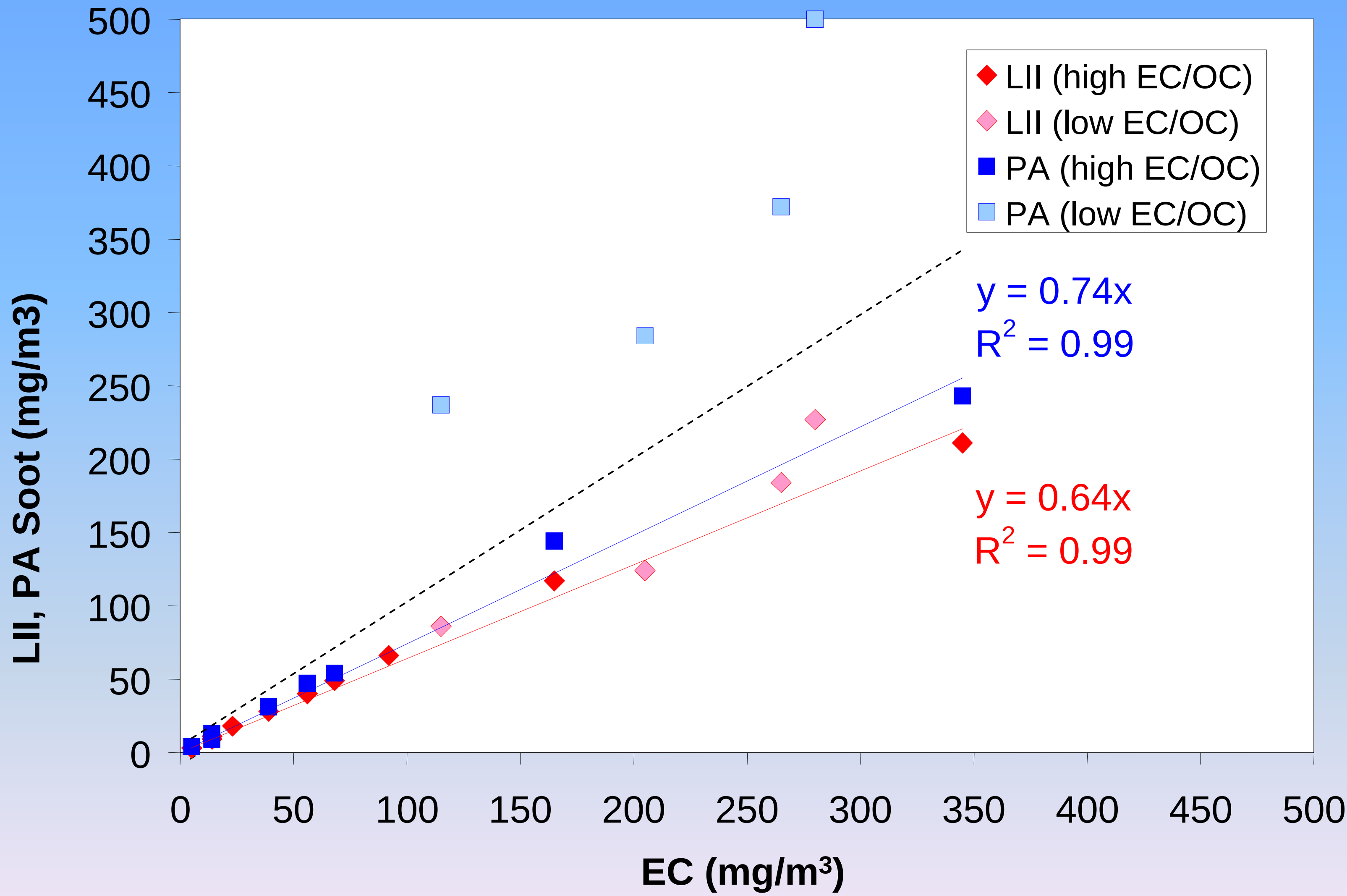
Cummins Instrument Comparisons

March 2010



Calibration Curve for Conventional LII-to-Mass



Kramer, of IAV, CRC 2006

Field Tests at the Port of Oakland Shipping Yards

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LII 300 Setup for Field Testing

Test Location – Port of Oakland Overpass to Shipyards

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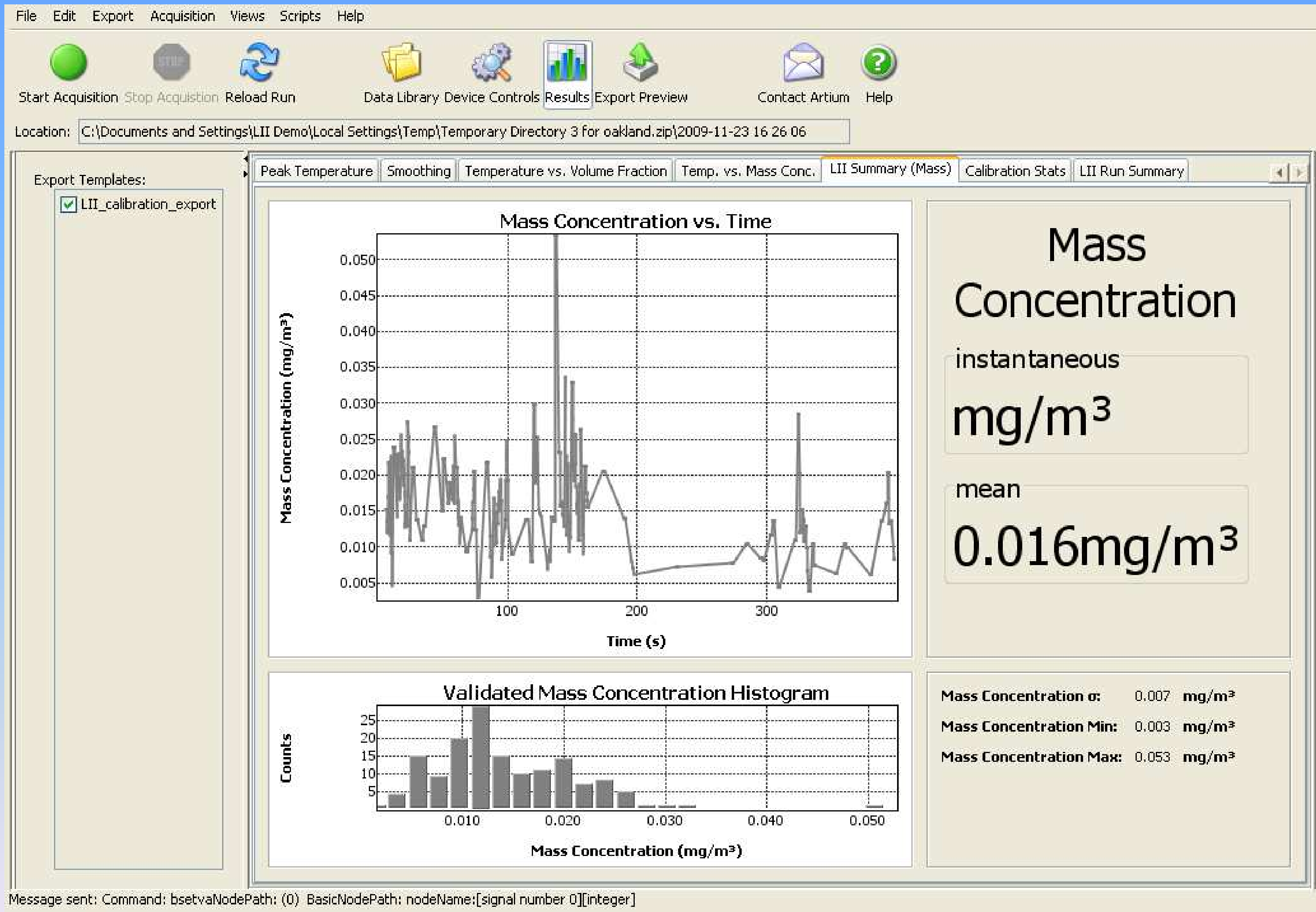
Atmospheric Sampling In Neighborhood of Port of Oakland

Artium Technologies Inc.

Sample Data From Oakland Shipyard Tests



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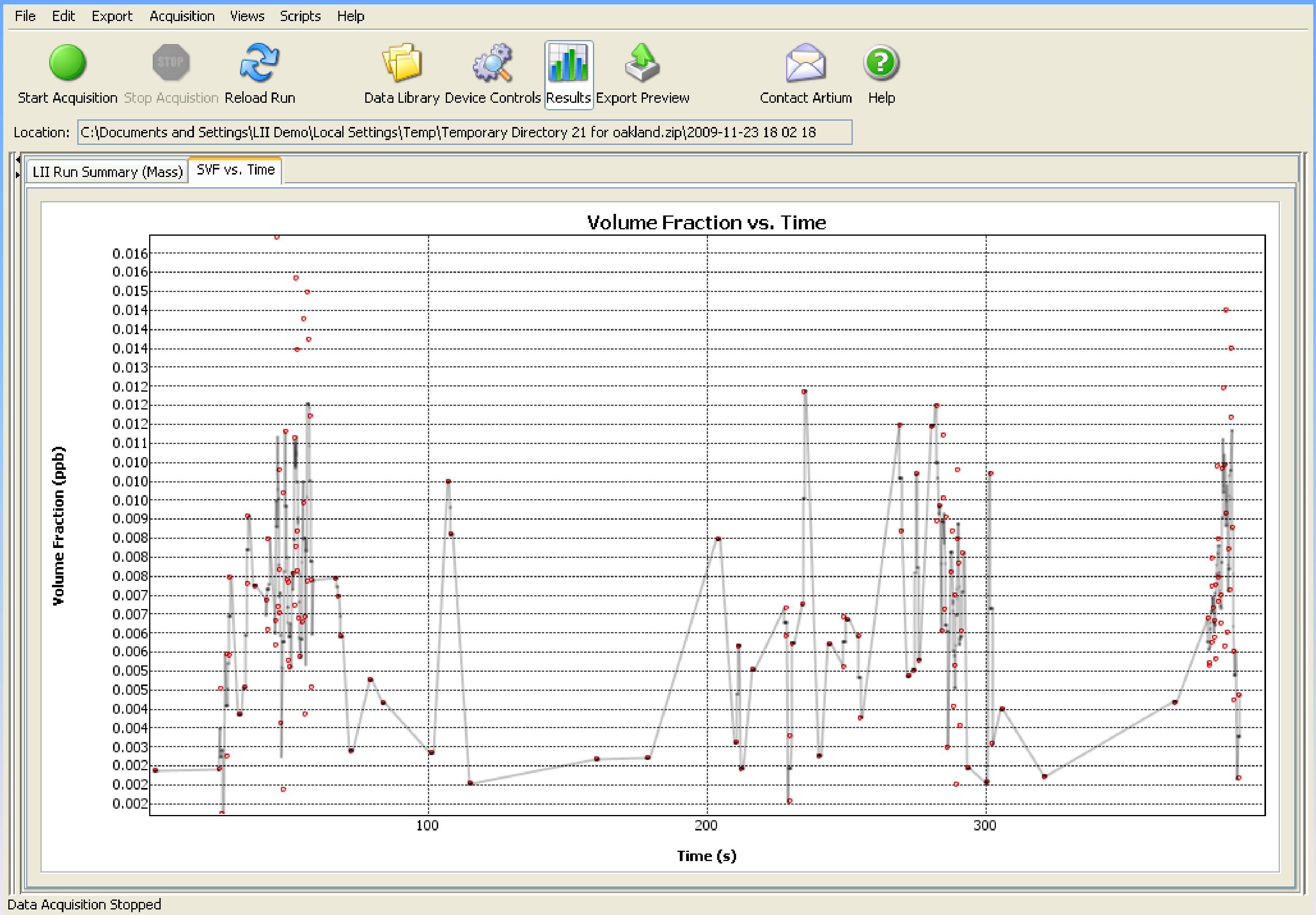
Variation of Soot Volume Fraction with Time (truck transits)



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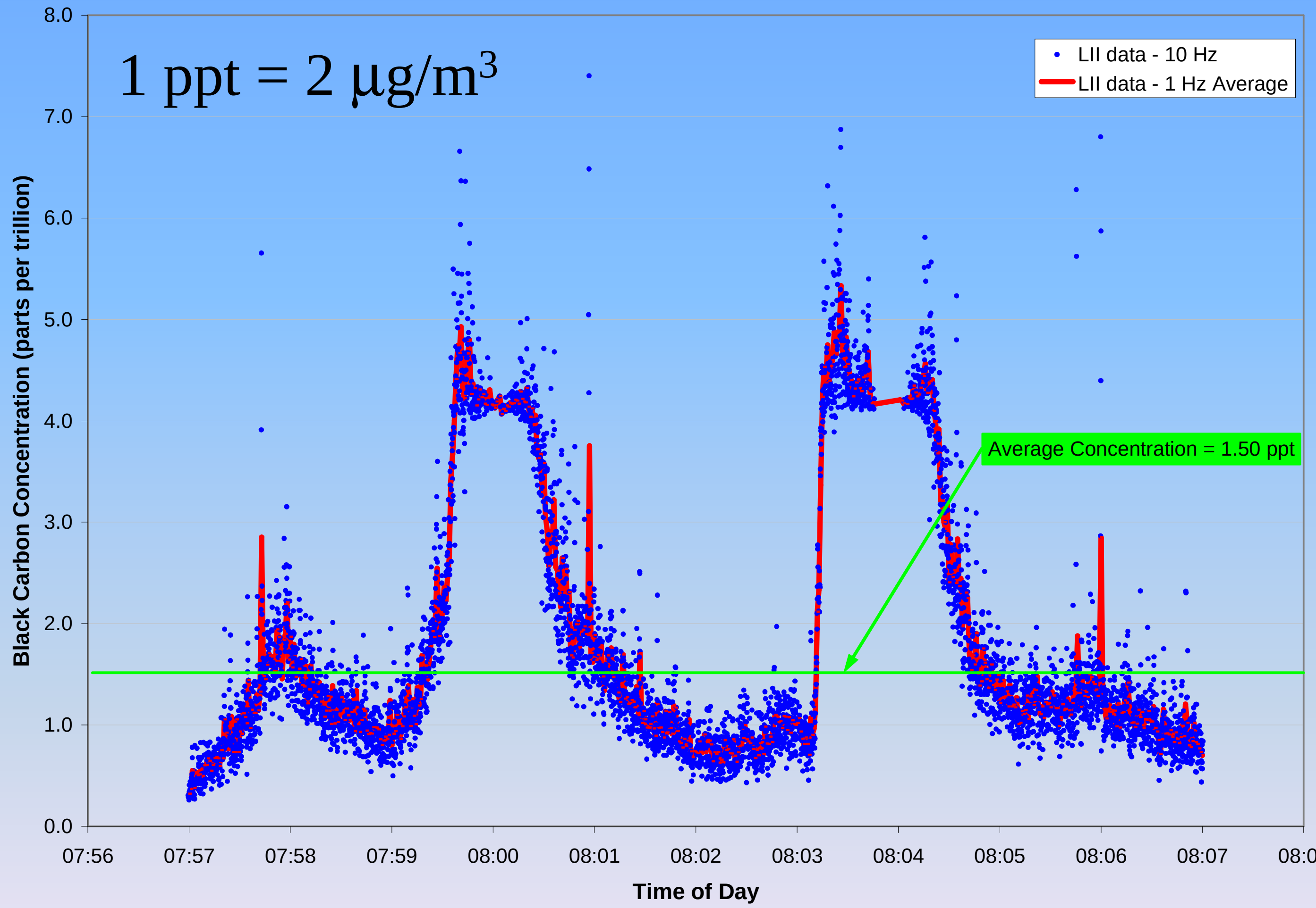
NRC Canada Very High Sensitivity LII



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Turbine Engine (Helicopter) Tests at Wright Patterson AFB

SAE E31

EPA
Filters

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Turbine Engine (Helicopter) Tests at Wright Patterson AFB
SAE E31

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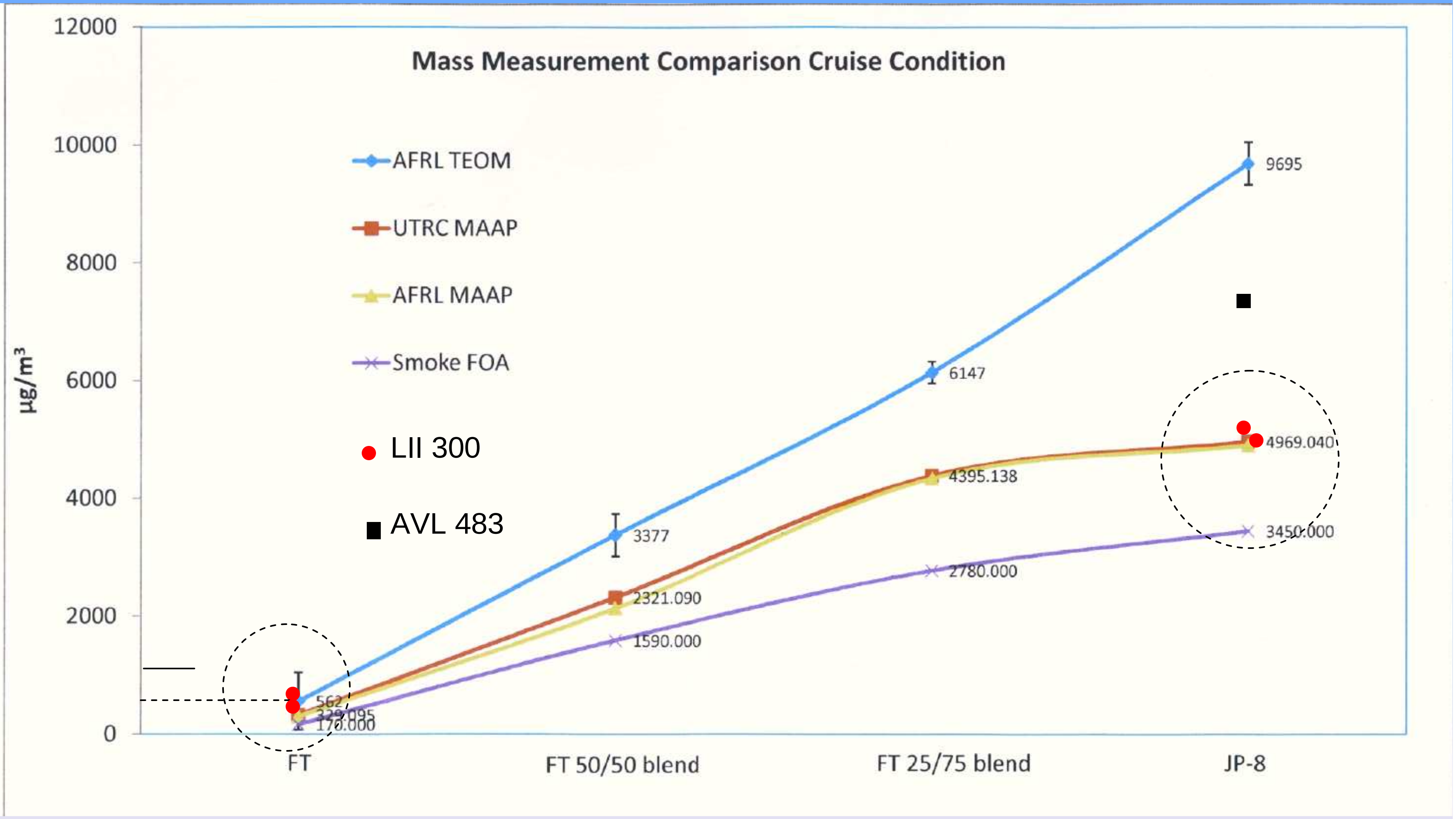
Data Acquired at Wright Patterson AFB (SAE E31)



FT – Fischer-Tropsch synthetic fuel, gas to liquids technology

Early Breadboard NRC LII Instrument

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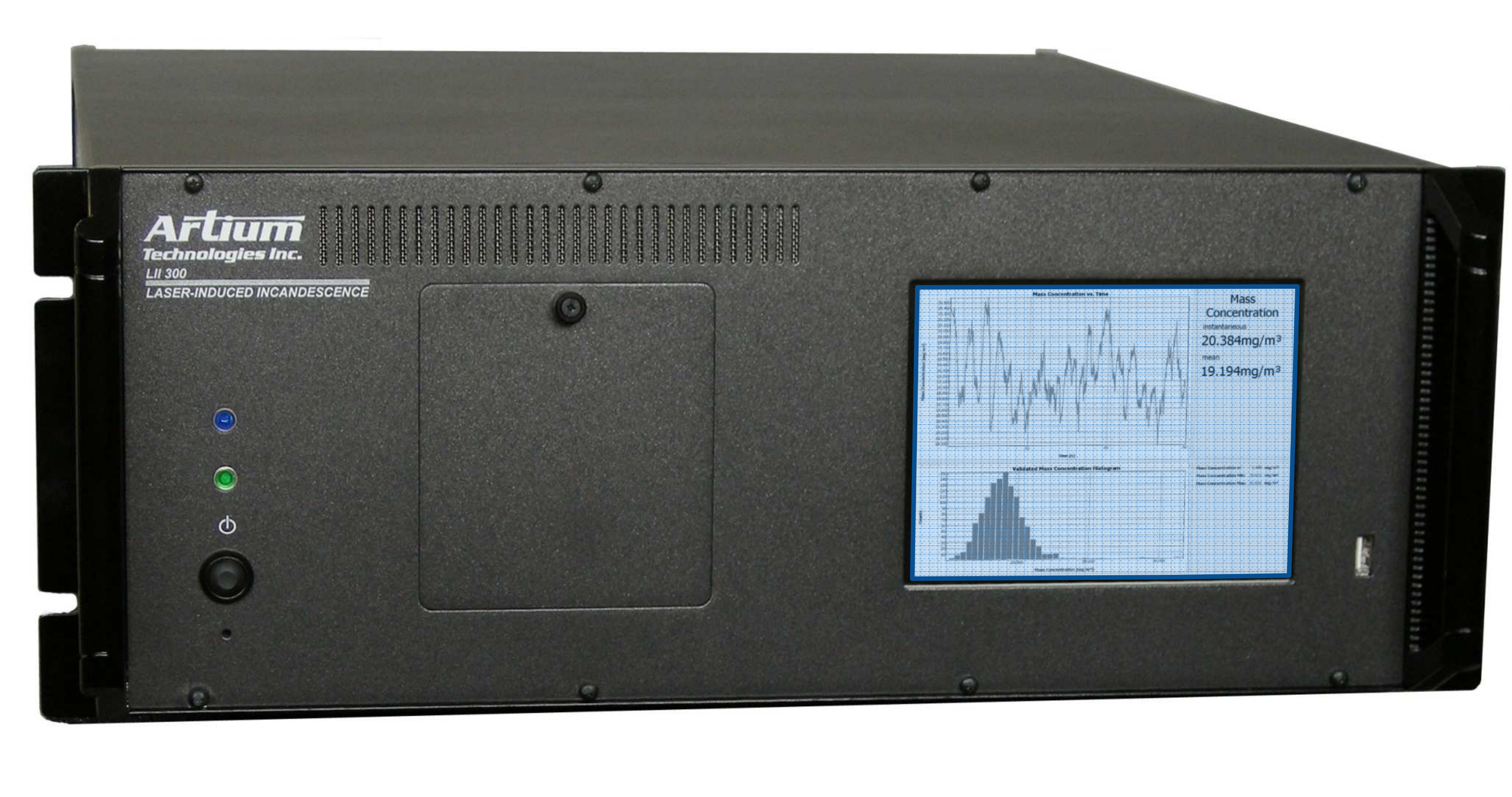
Technologies Inc.

LII 200 Developed for Lab Use

LII 300 LASER-INDUCED INCANDESCENCE
Instrument for Soot Characterization

Artium Technologies, Inc. provides the **LII 300** system, the most advanced laser-induced incandescence instrument available in the market today.



Measures Soot Concentration (mass or volume basis), Specific Surface Area, and Primary Particle Diameter in Real-Time

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Summary: LII Features

- *in situ* and nonintrusive
- signal is proportional to soot volume fraction
- spatially resolved measurements
- time resolved
- large measurement range
  - not limited by aggregate size
- high precision and repeatability
- high speed data acquisition and analysis

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Summary LII Benefits:

- dilution of sample not required
- stable measurement of elemental carbon
- insensitive to presence of other species
- can operate at very low concentrations
- real-time results
- cycle-resolved measurements possible
- can provide particulate morphology (size, size distribution, number density) when combined with scattering
- little maintenance required over extended periods of operation

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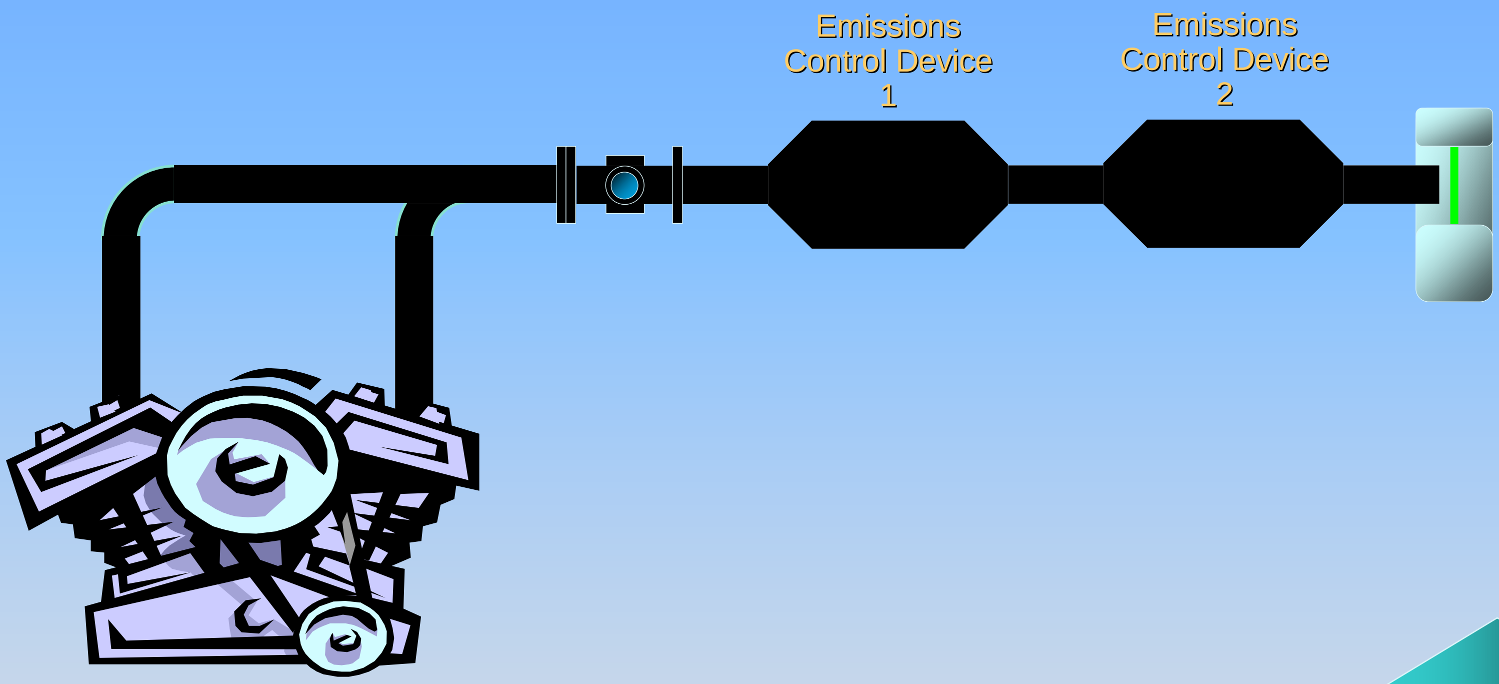
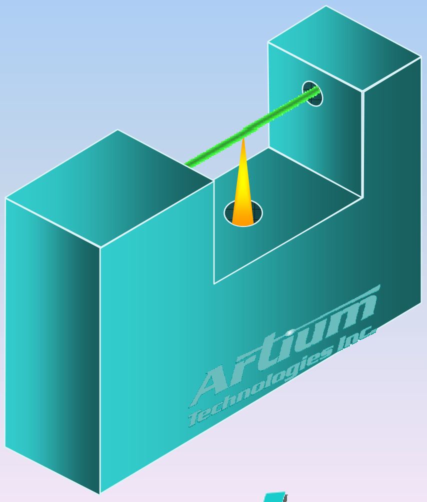
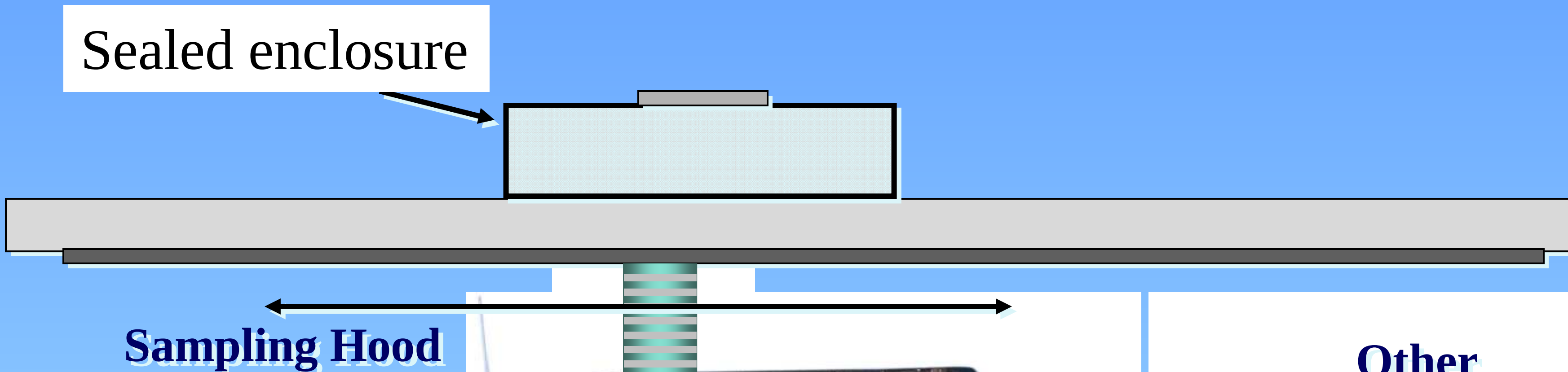
LII in Emissions Control Development





- LII provides sensitivity for post-2007 regulations (measures *microgram per cubic metre* concentration)
- Ideal for measuring engine-out / emissions-control-systems-in particulate levels
- Evaluate emissions control system efficiency

LII Particulate Monitoring Instrument



Develop, Evaluate, and Commercialize

Laser-Induced Incandescence (LII)

Systems for Online Exhaust Particulate Material (PM) Monitoring

Thanks for your attention!

Questions or Comments?

Thanks again for the
Development Support by California Air Resources Board
Innovative Clean Air Technology (ICAT) Grant 06-03

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Greg Smallwood, Ph.D. and David Snelling, Ph.D.
NRC Research supported in part by the
Program on Energy Research and Development (PERD)

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